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, \([\text{Ir}(ppy)_2(L)]PF_6\) (1), has been synthesized and structurally characterized. The absorption spectra, luminescent spectra and electrochemical behaviors of \(L\) and 1 have been investigated. Complex 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 3\(\pi\)–\(\pi^*\) and 3\(MLCT\) 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 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.

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\(H\)-1,2,3-triazol-4-yl)pyridine (L). Ligand L was used as the polyp-
2. Experimental

2.1. Materials and Measurements

2-(1-(2-((4′,5′-bis(methylthio)-1H-1,2,3-triazol-4-yl)thio)ethyl)-1H-1,2,3-triazol-4-yl)pyridine (L) was synthesized in our previous work, and an improved preparation method was used to synthesize the cyclometalated iridium(III) complex with ppy as C=N ligand, [Ir(ppy)2(L)]PF6 (1) (Scheme 1). Their electrochemical and photophysical properties are also investigated.

2.2. Synthesis of [Ir(ppy)2(L)]PF6 (1)

A mixture of a dimer [Ir(ppy)2]Cl2 (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 NH4PF6 (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. 1H NMR (400 MHz, CDCl3): δ 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) 13C NMR (100 MHz, CDCl3): δ 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–PF6]+. IR (cm−1): ν = 3442, 2922, 2853, 1608, 1475, 1422, 1265, 1100, 842, 756, 556; Anal. calcd. for C39H32F6IrN6P7S7: 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-Bu4NCIO4 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 (λ < 350 nm) are assigned to spin-allowed intraligand (π→π*) 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[6] and metal-to-ligand charge-transfer (MLCT, dπ(Ir)→π*(L)) transition for 1, respectively.[17,18]

3.1.2. Emission Properties

The relative emission spectra of ligand L and complex 1 in degassed CH2Cl2 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 499 nm. As for L, the emission band occurs at about 462 nm (λem = 462 nm). Therefore the vibronically structured emission of 1 is probably derived from a mixing of 3LC (3π→π*) and 3CT (3MLCT) excited states.[19,20]
try in CH₂Cl₂ 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⁺ and TTF₂⁺. Additionally, complex 1 show a irreversible oxidation peak (E_pox) at 1.88 V, which is attributed to the metal-centered Ir³⁺/Ir⁴⁺ oxidation couple. 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, 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.

Table 1: Redox potentials of ligand L and complex 1

<table>
<thead>
<tr>
<th>Compounds</th>
<th>E_{1/2}¹ (V)</th>
<th>E_{1/2}² (V)</th>
<th>E_pox (Ir³⁺/Ir⁴⁺) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.57</td>
<td>0.91</td>
<td>–</td>
</tr>
<tr>
<td>1</td>
<td>0.48</td>
<td>0.87</td>
<td>1.88</td>
</tr>
</tbody>
</table>

*E_p = 1/2(E_p + E_pc), where E_p and E_pc are the anodic and cathodic peak potentials, respectively.

Fig. 1: UV and FL spectra of ligand L and complex 1 in CH₂Cl₂

Fig. 2: Cyclic voltammograms for ligand L and complex 1 in CH₂Cl₂ solution containing n-Bu₄NClO₄ (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, ¹³C NMR, mass 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 (π→π* + MLCT) transitions. The electrochemical studies reveal that 1 undergo reversible TTF/TTF⁺/TTF₂⁺ redox processes and one irreversible Ir³⁺→Ir⁴⁺ oxidation process. The research plays a role in designing new photoelectric functional materials, and more work is going on in our laboratory.

5. Acknowledgements

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6. Supplementary Material

¹H NMR, ¹³C NMR and ESI-MS spectra for iridium complex 1.

7. References

Povzetek

Sintetiziran in strukturno okarakteriziran je nov iridijev(III) kompleks \([\text{Ir}(ppy)_2(L)]PF_6\) (1) z vezanim triazol-piridinskim ligandom modificiranim s tetratiafulvensko skupino. Absorpcijski in luminiscenčni spekter ter elektrokemijske lastnosti \(L\) in 1 so bili raziskani. Kompleks 1 emitira pri sobni temperature pri 481 in 510 nm. Interakcija iridijevskega iona na redoks lastnosti TTF skupine je bil raziskan s pomočjo ciklične voltametrije.