

Scientific paper

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

Zhi-Gang Niu, Hui Xie, Li-Rong He, Kai-Xiu Li, Qing Xia,
Dong-Min Wu, Gao-Nan Li*

College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou 571158, PR China

* Corresponding author: E-mail: ligaonan2008@163.com,
niuZHIGANG1982@126.com

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Abstract

A new iridium(III) complex based on the triazole-pyridine ligand with tetrathiafulvalene unit, $[\text{Ir}(\text{ppy})_2(\text{L})]\text{PF}_6$ (**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 ^3LC ($^3\pi-\pi^*$) and ^3CT ($^3\text{MLCT}$) excited states. The influence of iridium ion coordination on the redox properties of the TTF has also been investigated by cyclic voltammetry.

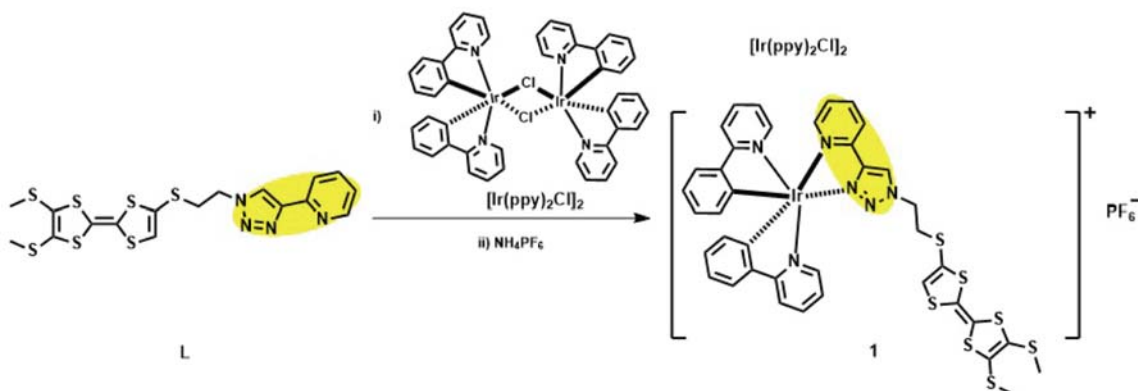
Keywords: Iridium(III) complexes; Tetrathiafulvalene; Triazole-pyridine ligands; Photoluminescence; Cyclic voltammetry

1. Introduction

For several decades, tetrathiafulvalene (TTF) and its derivatives were extensively developed by scientists in photofunctional materials^{1–8} 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.⁹

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



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

iridine N^N ligand and binap/xantphos as diphosphines P^P ligand to form two Cu(I) complexes, [Cu(I)(Binap)(L)]BF₄ and [Cu(I)(Xantphos)(L)]BF₄, which exhibited advantageous electrochemical and photophysical properties.¹⁰ The results hence led us to further design other metal complexes based on the TTF-containing thioethyl-bridged 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-cyclometalated TTF-based 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. Experimental

2.1. Materials and Measurements

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

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM 400 MHz instrument. Chemical shifts were reported in ppm relative to Me₄Si as internal standard. FT-IR spectra were taken on a Nicolet 6700 FTIR spectrometer (400–4000 cm⁻¹) 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)]PF₆ (**1**)

A mixture of a dimer [Ir(ppy)₂Cl]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 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 (m), 2922 (w), 2853 (w), 1608 (m), 1475 (m), 1422 (m), 1265 (w), 1100 (w), 842 (s), 756 (m), 556 (w). Anal. calcd. For C₃₉H₃₂F₆IrN₆PS₇: 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*-Bu₄NClO₄ 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**¹⁶ and metal-to-ligand charge-transfer (MLCT, $d\pi(\text{Ir}) \rightarrow \pi^*(\text{L})$) 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 510 nm. As for **L**, the emission band occurs at about 462 nm ($\lambda_{\text{ex}} = 363$ nm). Therefore the vibronically structured emission of **1** is probably derived from a mixing of ³LC (³ $\pi-\pi^*$) and ³CT (³MLCT) excited states.^{19,20}

3.2. Electrochemical Properties

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

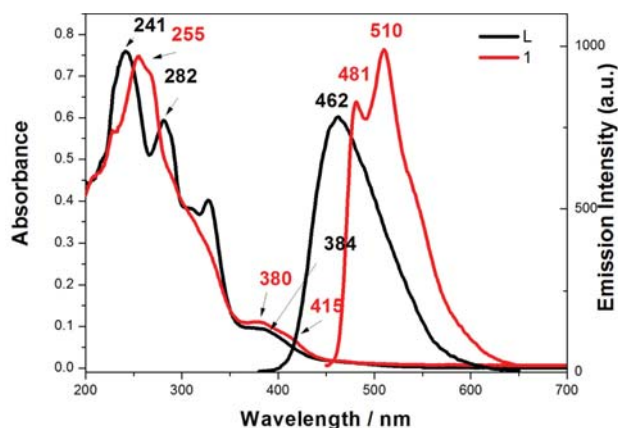


Fig. 1: UV and FL spectra of ligand **L** and complex **1** in CH_2Cl_2

try in 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^+ and TTF^{2+} . Additionally, complex **1** show a irreversible oxidation peak (E_p^{ox}) at 1.88 V, which is attributed to the metal-centered $\text{Ir}^{3+}/\text{Ir}^{4+}$ 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 **L** and complex **1**

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

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

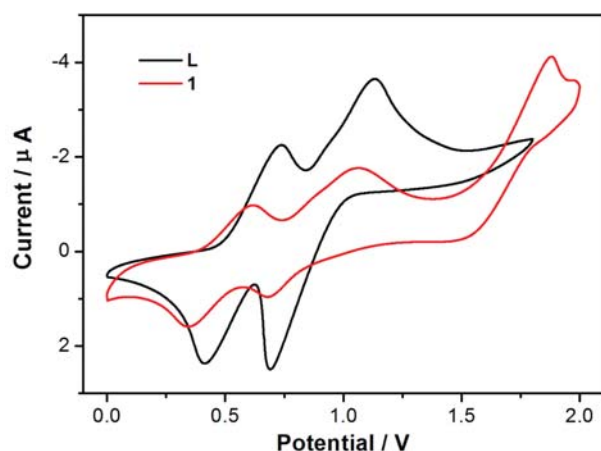


Fig. 2: Cyclic voltammograms for ligand **L** and complex **1** in CH_2Cl_2 solution containing $n\text{-Bu}_4\text{NClO}_4$ (0.1 M) at a sweep rate of 100 mV/s

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, ^{13}C 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 ($^3(\pi \rightarrow \pi^* + \text{MLCT})$) transitions. The electrochemical studies reveal that **1** undergo reversible $\text{TTF}/\text{TTF}^+/\text{TTF}^{2+}$ redox processes and one irreversible $\text{Ir}^{3+} \rightarrow \text{Ir}^{4+}$ 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, ^{13}C NMR and ESI-MS spectra for iridium complex **1**.

7. References

- M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891–4945.
<http://pubs.acs.org/doi/abs/10.1021/cr030666m>
- S. Wenger, P. A. Bouit, Q. L. Chen, J. Teuscher, D. D. Censo, R. H. Baker, J. E. Moser, J. L. Delgado, N. Martin, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2010**, *132*, 5164–5169.
<http://pubs.acs.org/doi/abs/10.1021/ja909291h>
- F. G. Brunetti, J. L. López, C. Atienza, N. Martín, *J. Mater. Chem.* **2012**, *22*, 4188–4205.
<http://pubs.rsc.org/en/content/articlepdf/2012/jm/c2jm15710a>
- D. Canevet, M. Sallé, G. X. Zhang, D. Q. Zhang, D. B. Zhu, *Chem. Commun.* **2009**, 2245–2269.
- Y. G. Sun, S. F. Ji, P. Huo, J. X. Yin, Y. D. Huang, Q. Y. Zhu, J. Dai, *Inorg. Chem.* **2014**, *53*, 3078–3087.
- G. N. Li, L. R. He, L. Li, W. F. Cheng, X. Y. Li, H. H. Chen, *Acta Chim. Slov.* **2014**, *61*, 786–791.
<https://journals.matheo.si/index.php/ACS/article/view/473>
- S. F. Ji, Y. G. Sun, P. Huo, W. C. Shen, Y. D. Huang, Q. Y. Zhu, J. Dai, *Inorg. Chem.* **2014**, *53*, 3611–3617.

8. J. Qin, L. Hu, N. Lei, Y. F. Liu, K. K. Zhang, J. L. Zuo, *Acta Chim. Slov.* **2014**, *61*, 740–745.
<https://journals.matheo.si/index.php/ACSi/article/view/443>
9. D. Lorcy, N. Bellec, M. Fourmigué, N. Avarvari, *Coordin. Chem. Rev.* **2009**, *253*, 1398–1438.
<http://www.sciencedirect.com/science/article/pii/S0010854508001768>
10. G. N. Li, L. R. He, D. Xia, L. Li, W. F. Cheng, K. X. Li, F. Cui, Z. G. Niu, *J. Chin. Chem. Soc.* **2015**, *62*, 889–897.
<http://onlinelibrary.wiley.com/doi/10.1002/jccs.201500251/abstract>
11. K. R. J. Thomas, M. Velusamy, J. T. Lin, C. H. Chien, Y. T. Tao, Y. S. Wen, Y. H. Hu, P. T. Tai, *Inorg. Chem.* **2005**, *44*, 5677–5685.
<http://pubs.acs.org/doi/abs/10.1021/ic050385s>
12. M. A. Baldo, C. Adachi, S. R. Forrest, *Phys. Rev. B.* **2000**, *62*, 10967–10977.
<http://journals.aps.org/prb/abstract/10.1103/PhysRevB.62.10967#fulltext>
13. J. M. Lupton, I. D. W. Samuel, M. J. Frampton, R. Beavington, P. L. Burn, *Adv. Funct. Mater.* **2001**, *11*, 287–294.
[http://onlinelibrary.wiley.com/doi/10.1002/1616-3028\(200108\)11:4%3C287::AID-ADFM287%3E3.0.CO;2-Z/abstract](http://onlinelibrary.wiley.com/doi/10.1002/1616-3028(200108)11:4%3C287::AID-ADFM287%3E3.0.CO;2-Z/abstract)
14. Y. P. Zeng, C. W. Gao, L. J. Hu, H. H. Chen, G. Y. Chen, G. N. Li, Z. G. Niu, *Acta Chim. Slov.* **2015**, *62*, 917–922.
<https://journals.matheo.si/index.php/ACSi/article/view/1744>
15. R. D. Costa, E. Ortí, H. J. Bolink, S. Graber, S. Schaffner, M. Neuburger, C. E. Housecroft, E. C. Constable, *Adv. Funct. Mater.* **2009**, *19*, 3456–3463.
<http://onlinelibrary.wiley.com/doi/10.1002/adfm.200900911/full>
16. G. N. Li, Y. Liao, T. Jin, Y. Z. Li, *Inorg. Chem. Commun.* **2013**, *35*, 27–30.
<http://www.sciencedirect.com/science/article/pii/S1387700313002153>
17. S. Okada, K. Okinaka, H. Iwawaki, M. Furugori, M. Hashimoto, T. Mukaide, J. Kamatani, S. Igawa, A. Tsuboyama, T. Takiguchi, K. Ueno, *Dalton Trans.* **2005**, *9*, 15–83.
<http://pubs.rsc.org/en/content/articlehtml/2005/dt/b417058j>
18. J. Qin, S. Y. Deng, C. X. Qian, T. Y. Li, H. X. Ju, J. L. Zuo, *J. Organomet. Chem.* **2014**, *750*, 7–12.
19. Z. G. Niu, D. Liu, J. Zuo, J. M. Yang, Y. H. Su, Y. D. Yang, G. N. Li, *Inorg. Chem. Commun.* **2014**, *43*, 146–150.
<http://www.sciencedirect.com/science/article/pii/S1387700314000872>
20. L. Y. Zhang, G. F. Liu, S. L. Zheng, B. H. Ye, X. M. Zhang, X. M. Chen, *Eur. J. Inorg. Chem.* **2003**, 2965–2971.
<http://onlinelibrary.wiley.com/doi/10.1002/ejic.200300061/abstract>
21. S. Bettington, M. Tavasli, M. R. Bryce, A. Beeby, H. A. Attar, A. P. Monkman, *Chem. Eur. J.* **2007**, *13*, 1423–1431.
<http://onlinelibrary.wiley.com/doi/10.1002/chem.200600888/citedby>
22. M. K. Nazeeruddin, R. T. Wegh, Z. Zhou, C. Klein, Q. Wang, F. D. Angelis, S. Fantacci, M. Grätzel, *Inorg. Chem.* **2006**, *45*, 9245–9250.
<http://pubs.acs.org/doi/abs/10.1021/ic060495e>
23. G. N. Li, T. Jin, L. Sun, J. Qin, D. Wen, J. L. Zuo, X. Z. You, *J. Organomet. Chem.* **2011**, *696*, 3076–3085.
<http://www.sciencedirect.com/science/article/pii/S0022328X11003676>

Povzetek

Sintetiziran in strukturno okarakteriziran je nov iridijev(III) kompleks $[\text{Ir}(\text{ppy})_2(\text{L})]\text{PF}_6$ (**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. Široki in strukturirani emisijski trakovi so pripisani mešanju ^3LC ($^3\pi-\pi^*$) in ^3CT ($^3\text{MLCT}$) vzbujenih stanj. Vpliv koordinacije iridijevega iona na redoks lastnosti TTF skupine je bil raziskan s pomočjo ciklične voltometrije.

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

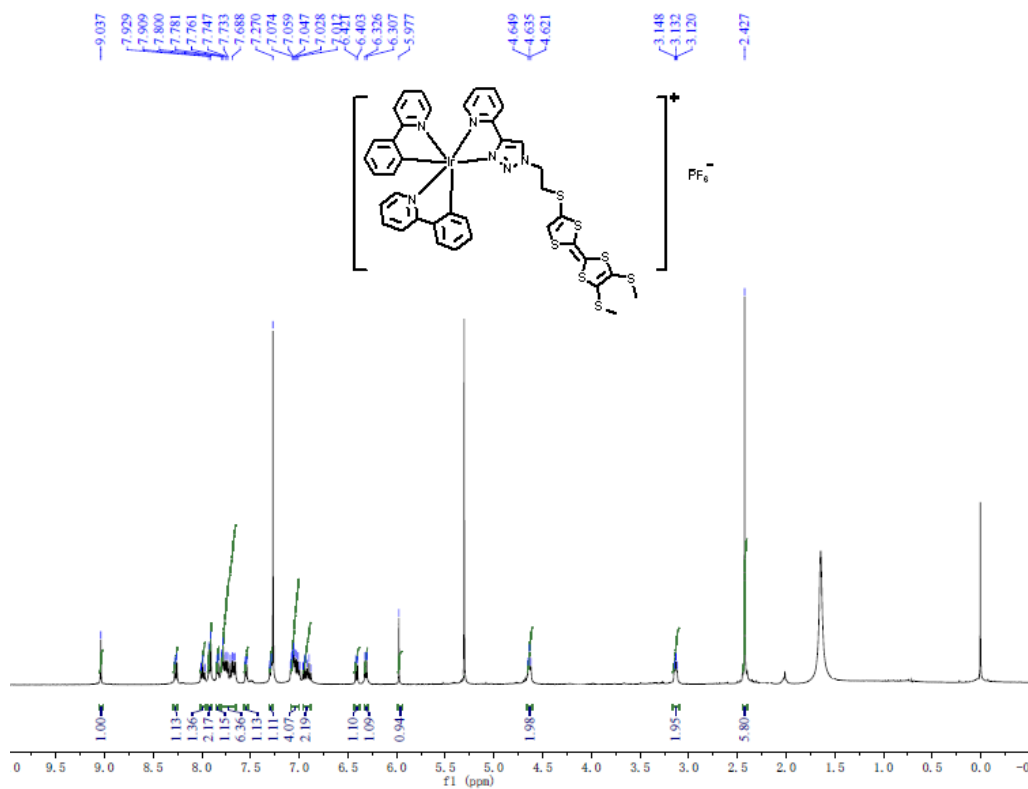
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Gao-Nan Li*

College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou 571158, PR
China

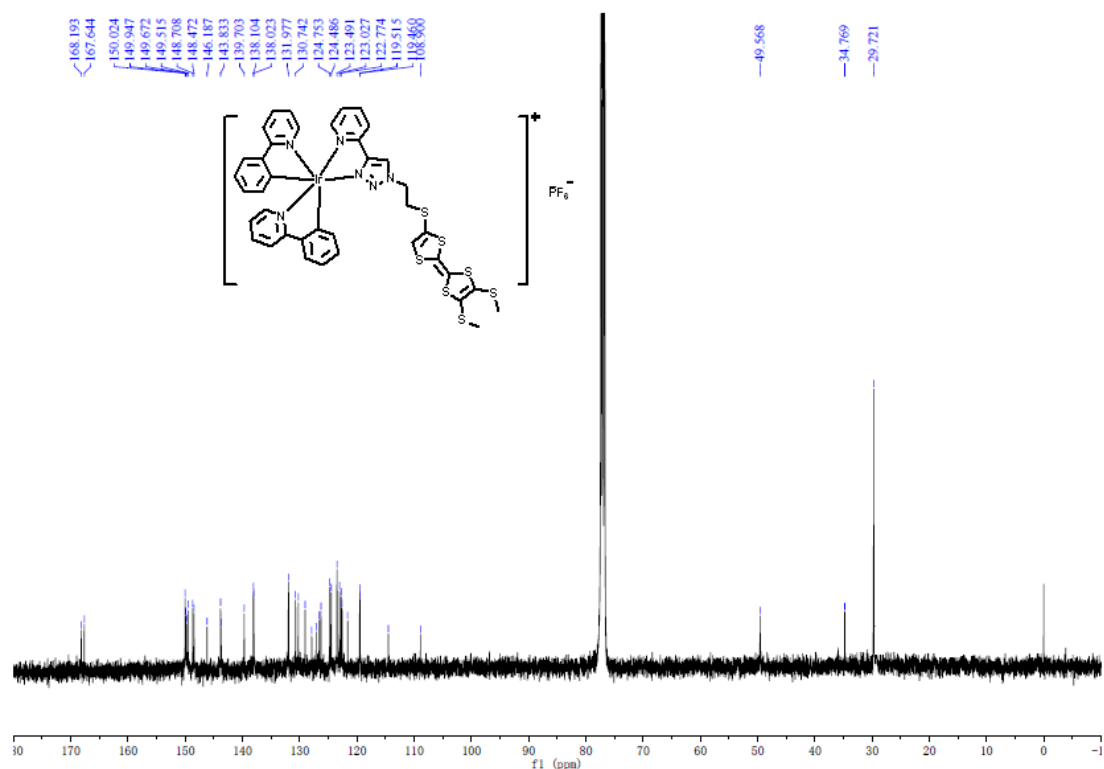
* Corresponding author: E-mail: ligaonan2008@163.com, niuzhigang1982@126.com

Supplementary Information

^1H NMR of Iridium Complex 1



¹³C NMR of Iridium Complex 1



ESI-MS of Iridium Complex 1

Mass Spectrum List Report

Analysis Info		Acquisition Date	
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Comment			
Acquisition Parameter			
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Capillary Exit	-166.0 Volt	Skimmer	-40.0 Volt
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