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

Received: 13-01-2016

Abstract

A new iridium(III) complex based on the triazole-pyridine ligand with tetrathiafulvalene unit, \([\text{Ir(ppy)}_2(\text{L})]\text{PF}_6 (1)\), has been synthesized and structurally characterized. The absorption spectra, luminescent spectra and electrochemical behaviors of \(\text{L}\) 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 \(3\pi^*\) and \(3\text{MLCT}\) 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\(^1\)\(^\text{--}\)\(^8\), 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-dithiolylidene)]-4-yl)thio)ethyl)-1H-1,2,3-triazol-4-yl)pyridine (\(\text{L}\)). Ligand \(\text{L}\) was used as the polyp-
yridine 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)(Xanthos)(L)]BF₄, which exhibited advantageous electrochemical and photophysical properties. The results hence led us to further design other metal complexes based on the TTF-containing thiophenol-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. Therefore, high phosphorescence quantum efficiency, long excited-state lifetime and excellent color tenability.11–14 Therefore, high phosphorescence quantum efficiency, long excited-state lifetime and excellent color tenability. Therefore, high phosphorescence quantum efficiency, long excited-state lifetime and excellent color tenability. Therefore, high phosphorescence quantum efficiency, long excited-state lifetime and excellent color tenability. Therefore, high phosphorescence quantum efficiency, long excited-state lifetime and excellent color tenability. Therefore, high phosphorescence quantum efficiency, long excited-state lifetime and excellent color tenability.

2. Experimental

2.1. Materials and Measurements

2-[(2-{4',5'-bis(methylthio)-[2,2'-bi(1,3-dithiolylidene)]-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 cyclo-metalated iridium(III) complex with ppy as C’N ligand, [Irppy]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, 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, 46.9, 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), 1381 (m), 1265 (w), 1100 (w), 842 (s), 756 (m), 556 (w). Anal. calcd. For C₆₃H₄₉F₆IrN₆P₇S₇: 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 results of the ligand L and complex 1 in dichloromethane solution 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 L⁴ and metal-to-ligand charge-transfer (MLCT, dπ(Ir)→π*(L)) transition for 1, respectively.⁴,⁷

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 (λₑₓ = 363 nm). Therefore the vibronically structured emission of 1 is probably derived from a mixing of °C*(π*–π*) and °CT (°MLCT) excited states.⁶,²⁰

3.2. Electrochemical Properties

The electrochemical behaviors of the ligand L and iridium complex 1 were investigated by cyclic voltamme-
try in CH$_2$Cl$_2$ 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 shows an irreversible oxidation peak ($E_{\text{p}^\text{ox}}$) at 1.88 V, which is attributed to the metal-centered Ir$^{3+}$/Ir$^{4+}$ 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

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

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

Fig. 2: Cyclic voltammograms for ligand L and complex 1 in CH$_2$Cl$_2$ solution containing n-Bu$_4$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 tetraphiafulvalene-substituted triazole-pyridine ligand, has been synthesized and fully characterized by $^1$H 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 ($\pi\to\pi^* +$ MLCT) transitions. The electrochemical studies reveal that 1 undergo reversible TTF/TTF$^+$/TTF$^{2+}$ redox processes and one irreversible Ir$^{3+}\to$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

This work was supported by the National Natural Science Foundation of China (No. 21501037), the Natural Science Foundation of Hainan Province (No. 20152031) and Hainan Provincial Innovation Experiment Program for University Students (No. 201511658002).

6. Supplementary Material

$^1$H NMR, $^{13}$C NMR and ESI-MS spectra for iridium complex 1.

7. References

1. M. Bendikov, F. Wudl, D. F. Perepichka, Chem. Rev. 2004, 104, 4891–4945. http://pubs.acs.org/doi/abs/10.1021/cr030666m
2. 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
3. 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
4. D. Canevet, M. Sallé, G. X. Zhang, D. Q. Zhang, D. B. Zhu, Chem. Commun. 2009, 2245–2269.
5. Y. G. Sun, S. F. Ji, P. Hao, J. X. Yin, Y. D. Huang, Q. Y. Zhu, J. Dai, Inorg. Chem. 2014, 53, 3078–3087.
6. 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/ACSJ/article/view/473
7. S. F. Ji, Y. G. Sun, P. Hao, 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. Fournigué, N. Avarvari, *Coord. 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.* **2014**, *61*, 740–745. 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/adfm.200100328/abstract
14. Y. P. Zeng, C. W. Gao, L. J. Hu, H. H. Chen, G. Y. Chen, G. N. Li, T. Jin, *Inorg. Chem. Commun.* **2013**, *16*, 27–30. http://www.sciencedirect.com/science/article/pii/S1387700313002153
15. S. Okada, K. Okinaka, H. Iwawaki, M. Furugori, M. Hashimoto, T. Mukae, 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
16. G. N. Li, Y. Liao, T. Jin, Y. Z. Li, *Inorg. Chem. Commun.* **2013**, *15*, 27–30. http://www.sciencedirect.com/science/article/pii/S1387700313002153
17. S. Okada, K. Okinaka, H. Iwawaki, M. Furugori, M. Hashimoto, T. Mukae, 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**, *15*, 14–150. 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 [Ir(ppy)$_2$($L$)]PF$_6$ (1) z vezanim triazol-piridinskih 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 emisijijski trakovi so pripisani mešanju 3LC ($\pi^*-\pi$) in 3CT (3MLCT) vzbujenih stanj. Vpliv koordinacije iridijevega iona na redoks lastnosti TTF skupine je bil raziskan s pomočjo ciklične voltametrije.