ATLANTIS PRESS

Advances in Engineering Research, volume 170

7th International Conference on Energy and Environmental Protection (ICEEP 2018)

Synthesis and Photophysical Properties of a Copper(I) Complex Emitting Material Containing 5-(9H-fluoren-2-yl)-2-(1H-imidazol-2-yl)Pyridine Ligand

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Keyword: Copper(I) complex, Fluorene, Photometric characterization, Luminescence.

Abstract. A new copper(I) complex of [Cu(Flu-im-Py)(POP)]PF_6 supported by Flu-im-Py =5-(9H-fluoren-2-yl)-2-(1H-imidazol-2-yl)pyridine, POP=bis(2-diphenylphosphanyl)ether, was synthesized and characterized. The corresponding photophysical properties were investigated using UV-vis and emission spectrometry. The weak absorption bands were observed in the region of 385-415 nm for complex [Cu(Flu-imPy)(POP)]PF_6, while the emission maximum was located at 583 nm upon excitation at 360 nm in PMMA films originating from the typical ^{3}MLCT excited state.

Introduction

Copper(I) complexes containing N-donor ligands have drawn special attention due to their structural diversities and rich photophysical properties as well as promising applications in numerous areas such as catalysis, organic light-emitting devices (OLEDs), dye-sensitized solar cells(DSSCs), optics and luminescent materials [1-3]. Compared with other noble metal complexes, Cu (I) complexes not only have lower cost and less toxicity, but also exhibit similar photophysical properties. However, the light absorption ability of Cu(I) complexes in the visible light region is limited. Their susceptibility to structural changes in the excited state and a subsequent non-radiative decay also result in low quantum yields [4,5]. Affected by these factors, it is considered worthwhile to design copper(I) complexes with high molar absorptivities and higher quantum yields.

2-(1H-imidazol-2-yl)pyridine, a five-membered nitrogen heterocyclic ligand, has been widely used in transition metal Cu(I) complexes due to its strong coordination ability and efficient emission quantum efficiency[7]. This ligand is employed in this paper since the steric and electronic properties of 2-(1H-imidazol-2-yl)pyridine can been modified by changing the substituents at the C5 position of the pyridine [8].

Fluorene is an excellent candidate for luminescence, which has biphenyl structure with rigid plane, as well as large π-conjugated system. Highly rigid structures of fluorene compounds endow their distinct photoelectric properties [9] and high thermal stability. Herein a new Cu(I) complex containing pyridine imidazol ligand incorporated with fluorene moiety was synthesized and characterized. The corresponding photophysical properties were discussed in detail.

Experimental

General. All the chemicals and solvents were obtained from commercial suppliers and used without futher purification.^{1}H NMR spectra were performed in an Burker AV400MHz spectrometer, using tetramethylsilane(TMS) as intermal reference. UV-vis absorption spectra were measured using a Perkin Elmer Lambda-900 spectrophotometer. Fluorescence spectra were determined with a Hitachi F-4600 Fluorescence spectrophotometer.

Synthetic Procedures.

2-(9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane(b)

(a;1.05 g,4.12 mmol), bis(pinacolatodiboron) (1.92 g,6.59 mmol),and potassium acetate (1.21 g,12.36 mmol) were placed in a 100 mL round bottom flask. Anhydrous dioxane (40 mL) and [PdCl2 (dppf)] (0.48 g,0.66 mmol) were added to the flask and the reaction vessel was degassed. The mixture was stirred at 80 °C for 12 h under nitrogen. After the mixture had been cooled to

room temperature, dioxane was removed by rotary evaporation. The residue was extracted with dichloromethane, and the organic phase was washed with water and brine, and dried over magnesium sulfate. The solvent was removed and the residue was purified by silica gel column chromatography(DCM/PE=1:2) to afford b (2.02 g,68%) as white crystals. ^{1}H NMR (400 MHz, DMSO) δ 7.92 (dd, *J* = 9.8, 6.1 Hz, 3H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 1H), 7.48 – 7.24 (m, 2H), 3.94 (s, 2H), 1.32 (s, 12H).

5-(9H-fluoren-2-yl)picolinaldehyde(c)

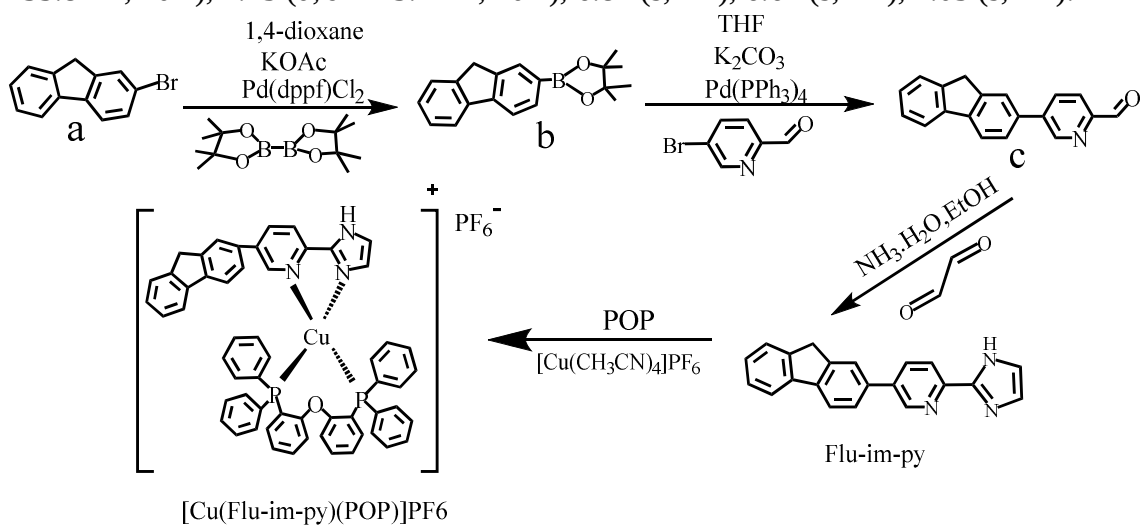
(5-bromopyridin-2-yl)methylene)oxonium (0.84 g, 4.52 mmol), Pd(PPh3)4 (0.38 g, 0.33 mmol) were added to a 20 mL THF solution. Then, Anhydrous ethanol 10 mL and 2 M K_2CO_3 solution (15 mL) dissolved in H_2O was added to the reaction mixture at 50 °C. (b; 1.94 g, 6.64 mmol) were added after half an hour and The mixture was refluxed for 5 h under nitrogen. After the reaction had finished, the mixture was filtered. The product was isolated using silica gel column chromatography with PE and EtAc (5:1)as the solvent. The solvent was removed by evaporation. Recrystallization of the residue from EtOH afforded a beige compound (1.69 g, 61%). ^{1}H NMR (400 MHz, DMSO) δ 10.05 (s, 1H), 9.24 (d, *J* = 2.0 Hz, 1H), 8.41 (dd, *J* = 8.1, 2.1 Hz, 1H), 8.17 – 7.96 (m, 4H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.41 (dt, *J* = 22.9, 7.2 Hz, 2H), 4.04 (s, 2H).

5-(9H-fluoren-2-yl)-2-(1H-imidazol-2-yl)pyridine(Flu-im-Py)

Anhydrous ethanol(25 mL) , glyoxal solution(5 mL) were stirred in an ice bath, Then,(c; 1.41 g, 5.22 mmol) and concentrated ammonia were added to the mixed solution under nitrogen for 1 h. The mixed solution was cooled to room temperature and allowed to stand for 12 h, extracted with dichloromethaned and washed by water until neutral, and evaporated under reduced pressure to remove the solvent. The product was isolated using silica gel column chromatography with EtOAc as the solvent. Recrystallization of the residue from EtOH afforded a brown compound (1.23 g, 41%). 1H NMR (400 MHz, DMSO) δ 8.99 (s, 1H), 8.25 (d, J = 8.3 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 7.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.44 – 7.32 (m, 2H), 7.20 (s, 1H), 7.06 (d, J = 19.4 Hz, 2H), 4.02 (s, 2H).

Synthesis of[Cu(Flu-im-Py)(POP)]PF_6

[$Cu(CH_3CN_4)$](PF_6)(0.124 g, 0.4mmol) and POP (0.216 g, 0.4 mmol) reacted in dichloromethane (15 mL) at 25°C for 2 h. Then, (Flu-im-Py) ligand (0.4 mmol) was dissolved in the degassed dichloromethane solution and injected into the mixed solution for 2 h. The resulting mixture was filtered through a plug of celite and concentrated to ca. 1 mL. Addition of Et_2O (10 mL) to the filtrate afforded a pale yellow precipitate, which was collected and washed with Et_2O. And the product was recrystallized with ethanol. The product was a yellow powder. Yield: 0.19 g, 58%. ^{1}H NMR (400 MHz, DMSO) δ 8.45 (s, 1H), 8.27 (d, *J* = 26.3 Hz, 2H), 7.98 (s, 2H), 7.65 (s, 3H), 7.45 (d, *J* = 55.8 Hz, 20H), 7.13 (d, *J* = 45.7 Hz, 10H), 6.81 (s, 4H), 6.67 (s, 2H), 4.03 (s, 2H).



Synthesis of the Flu-im-py and [Cu(Flu-im-Py)(POP)]PF_6

Results and Discussion

Synthesis.

The synthesis pathways of the ligand 5-(9H-fluoren-2-yl)-2-(1H-imidazol-2-yl)pyridine (Flu-im-Py) and Cu(I) complex [Cu(Flu-im-Py)(POP)]PF6 were shown in Scheme 1. 5-(9H-fluoren-2-yl)picolinaldehyde was synthesized according to a modified literature procedure[11].Ligand and complex were prepared by a condensation reaction according to the literature procedure[12].

UV-Vis Spectra.

Fig.1 UV-Vis absorption spectra of complex [Cu(Flu-im-Py)(POP)]PF_6 in CH_2Cl_2 solution with a concentration of 1×10^{-5} mol/L. The exhibit broad and intense absorption bands between 320–348nm(ε=2.4-2.6$\times10^4 M^{-1}cm^{-1}$) was exhibited, which can be attributed to ligand-centred (LC) transitions of the POP and (Flu-im-py) ligands. Additional shoulders (peak at 385−408 nm), which are not observed for the free ligands, can be attributed to metal-to-ligand charge-transfer (MLCT) transitions(ε=1.9-5.3$\times10^3 M^{-1}cm^{-1}$).

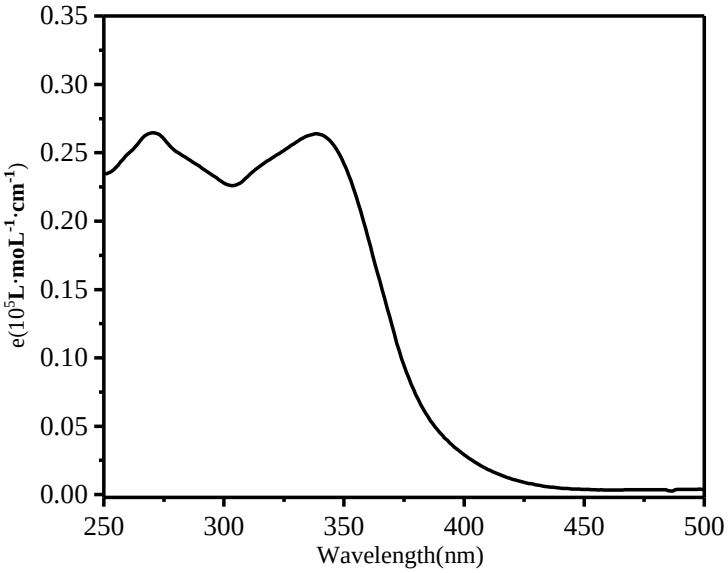


Figure 1. UV-vis absorption spectra of [Cu(Flu-im-Py)(POP)]PF_6 in 10^{-5}mol/L CH_2Cl_2 solution at room temperature.

Emission Spectra.

As indicated in Fig 2, a broad and structureless emission spectra of [Cu(Flu-im-Py)(POP)]PF_6 from a metal-to-ligand charge transfer (^{3}MLCT) excited states occur in the visible region 583 nm at room temperature in PMMA film.

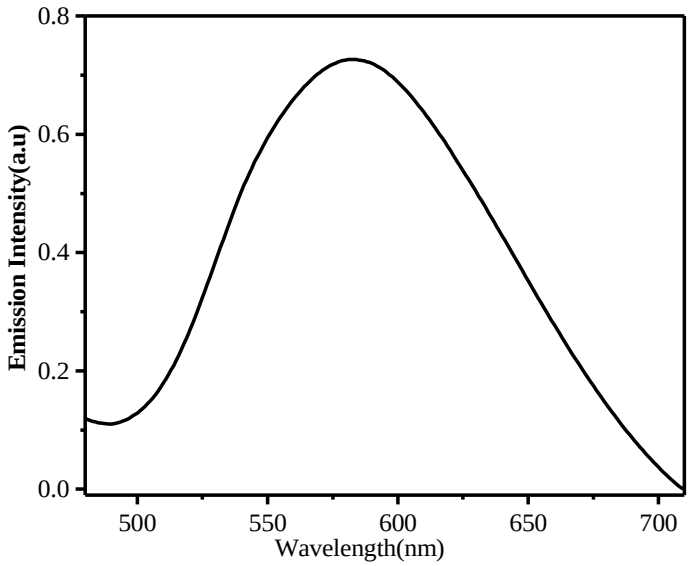


Figure 2. Emission spectra of [Cu(Flu-im-Py)(POP)]PF_6 (λ_{ex} = 360nm in PMMA film).

Conclusions

In this paper, A new copper(I) complex, [Cu(Flu-im-Py)(POP)]PF_6 was synthesized and characterized. In UV-Vis absorption spectra, [Cu(Flu-im-Py)(POP)]PF_6 has a additional absorption band at 385 nm. The emission spectrum of [Cu(Flu-im-Py)(POP)]PF_6 exhibits broad emission band centered at 583 nm at room temperature in PMMA film.

Acknowledgments

The work was supported by the national Natural Science Foundation of China (Nos.21462020 and 21563013),Jiangxi Science and Technology Normal University Key Laboratory of Organic-Inorganic Composite Materials (Key training base),and the Natural Science Foundation of Jiangxi Province(No.20151BAB203006)

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