Synthsis and Photophysical Properties of a copper (I) complex emitting material containing 1-(9H-fluoren-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline ligand

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Abstract. A new copper(I) complex, [Cu(βFlu-imPhen)(POP)]PF_6, where β-Flu-imPhen = 1-(9H-fluoren-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline , 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 350-400nm for complex [Cu(βFlu-imPhen)(POP)]PF_6, while the emission maximum was located at 584 nm upon excitation at 320 nm in PMMA films.

Introduction

Copper(I) complexes have received considerable attention and have been promising candidates for applications as emitting materials in organic light emitting diodes(OLEDs)[1-4].There are some advantages for Cu(I)complexes, including their low cost, earth abundancy, and few toxic properties. Furthermore, Cu(I) complexes show some photophysical properties similar to those of ruthenium(II) complexes that are widely used for solar conversion, OLED, photocatalysis, and so on[5-8].However the most Cu(I) complexes have the distorted tetrahedral geometries and readily suffer the Jahn-Teller distortions in the excited state[9,10], which results in the subsequent nonradiative decay and low quantum yields[11,12].

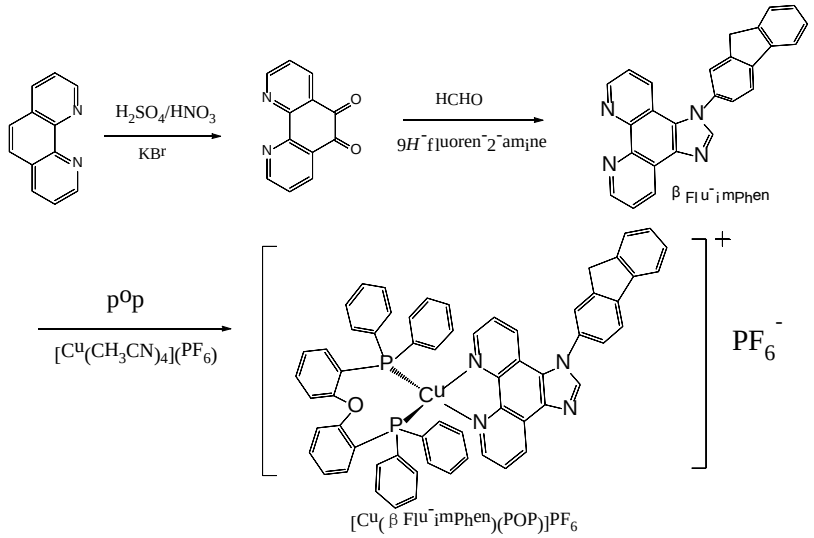
1H-imidazo[4,5-f][1,10]phenanthroline (imPhen), a nitrogen-containing heterocyclic compound, has been extensively used as a basic ligand to prepare the transition metal complexes due to its strong coordination ability and rigid planar skeleton.[13,14]We chose ligand imphen because one can adjust the steric and electronic properties of imphen by changing the substituents at the N1 and C2 position of the imidazole[15,16].

Fluorene, consisting of biphenyl units with rigid and planar structure, is a robust materials used as an active component due to its unique photophysical properties ,such large band gaps,π-donating ability, high emission efficiency and high thermal stability[17].Herein a new Cu(I) complex containing imPhen ligand incorporated with fluorene moiety was synthesized and characterized. The corresponding photophysical properties were discussed in detail.

Results and Discussion

Synthesis.

The synthesis pathways of the ligand βFlu-imPhen and Cu(I) complex [Cu(βFlu-imPhen)(POP)]PF_6 were shown in Scheme 1. 1,10-phenanthroline-5,6-dione was synthesized according to a modified literature procedure[18]. Ligand and complex were prepared by a condensation reaction according to the literature procedure[19].



Scheme 1 Synthesis of the βFlu-imPhen and [Cu(βFlu-imPhen)(POP)]PF_6

UV-Vis Spectra.

Fig.1 shows the UV-Vis absorption spectra of the βFlu-imPhen ligand and complex [Cu(βFlu-imPhen)(POP)]PF_6 in CH_2Cl_2 solution with a concentration of 1×10^{-5} mol/L. It can be observed that the shapes of the absorption spectra are generally similar to each other. But [Cu(βFlu-imPhen)(POP)]PF_6 has a additional absorption band at 350nm, which is characteristic ofmetal-to-ligand charge-transfer (MLCT) transitions.

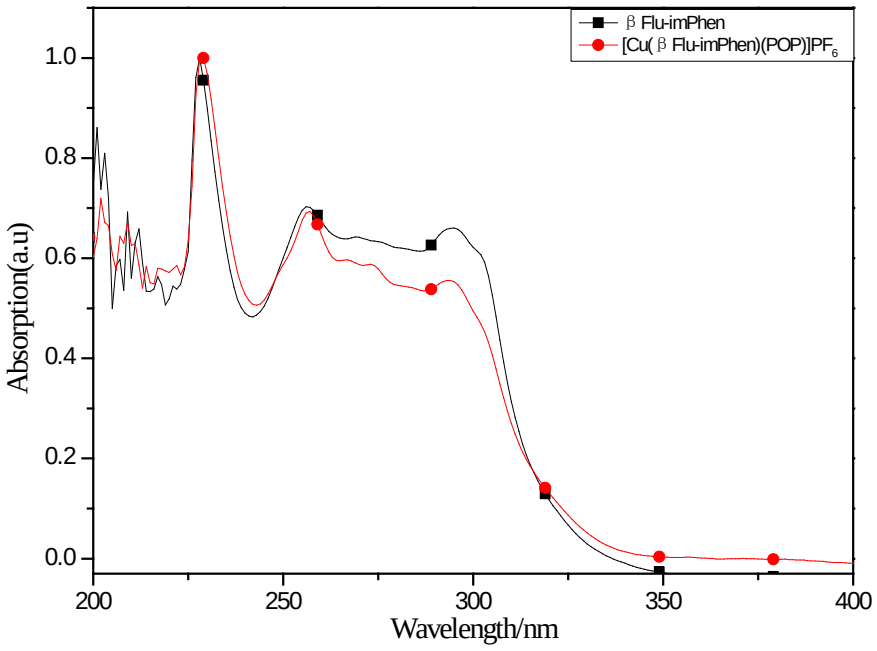


Figure 1.UV-vis absorption spectra of βFlu-imPhenand [Cu(βFlu-imPhen)(POP)]PF_6in 10^{-5}mol/L CH_2Cl_2 solution at room temperature.

Emission Spectra.

As indicated in Fig 2,the emission spectrum of [Cu(βFlu-imPhen)(POP)]PF_6exhibits broad emission band centered at 584 nm at room temperature in PMMA film arising from a metal-to-ligand charge transfer (^{3}MLCT) transition. In 1×10^{-5} mol/LCH_2Cl_2 solutions, the ligand βFlu-imPhen exhibits emission peak at 443 nm at room temperature.

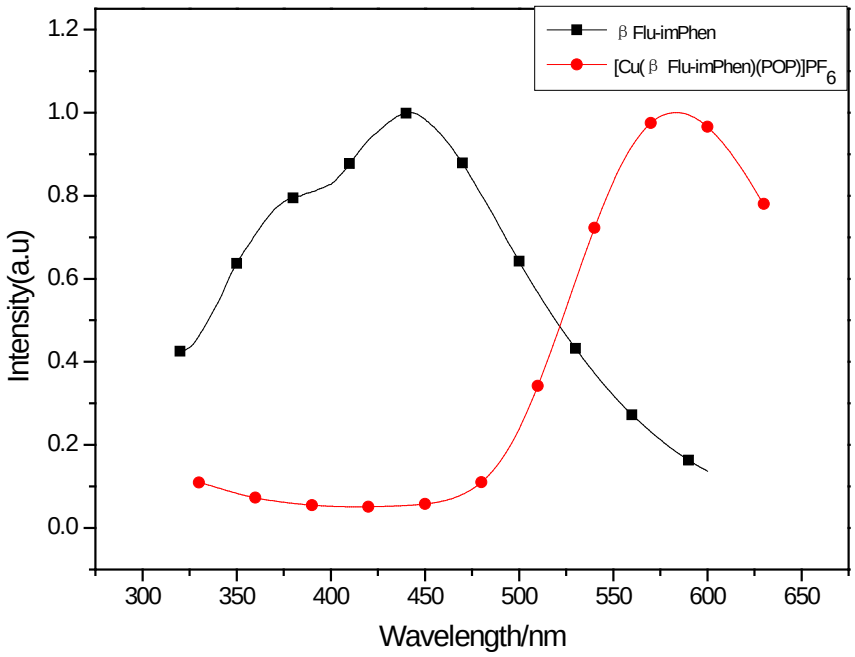


Figure 2.Emission spectra of βFlu-imPhen (λ_{ex} = 310nm in CH_2Cl_2solution) and [Cu(βFlu-imPhen)(POP)]PF_6 (λ_{ex} = 320nm in PMMA film).

Experimental

Materials.

1,10-Phenanthroline ,9H-fluoren-2-amine, polyoxymethylene, potassium bromide, ammoniumacetate, concentrated sulfuricacid and nitric acid ,anhydrous magnesiumsulfate, sodium hydroxide.were purchased from Sinopharm Chemicsl Reagent Co and used without further purification. All solvents were analytical grade reagents.

Characterization.

^{1}H NMR spectra were performed in an Burker AV400MHz spectrometer, using tetramethylsilane(TMS) as internal reference. UV-vis absorption spectra were measured using aPerkin Elmer Lambda-900 spectrophotometer. Fluorescence spectra were determined with a Hitachi F-450 Fluorescence spectrophotometer.

Synthetic Procedures.

1-(9H-fluoren-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline(βFlu-imPhen)

All reaction in N_2,all solvent must be degassed. Pour solid paraformaldehyde (0.030g,1mmol),9H-fluoren-2-amine (0.1812g,1mmol) and 20 ml glacial acetic acid into the 50ml three-necks flask. Stirring ten minutes at room temperature to get the yellow solution. Then, add 1,10-phenanthroline-5,6-dione(0.21g,1mmol) and ammonium acetate(0.77g,10mmol,excess) into the mixture . The mixture was stirred for 24h at 117 ℃.Then the solution was poured into the 200ml ice water and neutralized with Concentrated ammonia wateruntil the pH=7. The solution were extracted with CH_2Cl_2,dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated under reduced pressure to get yellow oily substance. Adding a little of acetone and 20 ml CH_2Cl_2, evaporate the acetone under reduced pressure(control the temperature under 30 ℃).Place the rest of solution in the refrigerator, after 2h ,filtering to get yellow solid(0.25g,60.0%) ^{1}H NMR (400 MHz, DMSO) δ 10.81 (s, 1H), 9.21 (d, *J* = 74.7 Hz, 1H), 9.09 (d, *J* = 3.3 Hz, 1H), 8.98 (d, *J* = 5.6 Hz, 2H), 8.56 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 7.4 Hz, 1H), 7.98 (s, 1H), 7.86 (dt, *J* = 24.7, 12.3 Hz, 1H), 7.77 (t, *J* = 7.0 Hz, 2H), 7.70 (d, *J* = 7.3 Hz, 1H), 7.57 – 7.36 (m, 3H), 4.11 (d, *J* = 7.9 Hz, 2H).

Synthesis of[Cu(βFlu-imPhen)(POP)]PF_6

All reaction in N_2 , all solvent must be degassed. Pour tetrakis(acetonitrile)copper(I) hexa-fluorophosph (0.031g,0.1mmol), (oxybis(2,1-phenylene))bis(diphenylphosphine) (POP) (0.054g,0.1mmol) and 10 ml CH_2Cl_2 into 50 ml round flask. Stirring 2 hours at room temperature. Then 0.2 mmol(0.077g) of ligand dissolved in CH_2Cl_2 after degassing treatment, injected into the above solution .Stirring 2 hours at room. Then the solution was filter by diatomite. The solvent was evaporated under reduced pressure to get yellow solid substance. Adding a little of CH_2Cl_2 and 20 ml ether, filtering to get yellow solid(0.0650g,40.1%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 7.9 Hz, 1H), 8.87 (s, 1H), 8.79 (d, *J* = 6.1 Hz, 2H), 8.28 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 6.9 Hz, 1H), 8.03 (s, 1H), 7.92 (dd, *J* = 18.8, 8.2 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 4.5 Hz, 1H), 7.53 – 7.40 (m, 4H), 7.33 (d, *J* = 24.4 Hz, 6H), 7.20 (s, 9H), 7.08 (d, *J* = 7.4 Hz, 2H), 6.96 (s, 7H), 6.64 (s, 2H), 4.12 (s, 2H).

Summary

In this paper, A new copper(I) complex, [Cu(βFlu-imPhen)(POP)]PF_6 was synthesized and characterized. In UV-Vis absorption spectra,[Cu(βFlu-imPhen)(POP)]PF_6 has a additional absorption band at 350nm compare with ligands βFlu-imPhen. The emission spectrum of [Cu(βFlu-imPhen)(POP)]PF_6exhibits broad emission band centered at 584 nm at room temperature in PMMA film.

Acknowledgments

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