

Synthesis and Photophysical Properties of Four-Coordinate N-heterocyclic Carbene Copper(I) Complex Emitting Material with Brightly Luminescence

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Abstract. A four-coordinate copper(I) complex containing N-heterocyclic carbene (NHC) ligand and bis([2-diphenylphosphino]-phenyl)ether (POP) ligand were successfully reported and characterized. The corresponding photophysical properties were investigated using UV-vis and emission spectrometry. The lowest-energy absorption band at 343 nm was assigned to metal-to-ligand charge transfer (MLCT) transition. The emission maximum located at 552 nm upon excitation at 290 nm in PMMA films at room temperature originates from the typical ³MLCT excited state.

Introduction

Up to now, there have been many reports on N-heterocyclic carbene (NHC) complexes (such as Ir, Pt), which have excellent photophysical properties and have been widely used [1-3]. However, disadvantages of these complexes, such as high cost, limited availability, limit the commercialization of phosphorescent OLEDs. N-heterocyclic carbene (NHC) copper(I) complexes have been studied because of their inexpensive cost and relatively low toxicity [4-8].

In 2009, Tsubomura group reported a complex [Cu₂(u-Me-mbim)₂](PF₆) exhibiting the blue-green luminescence with the quantum yield of 0.43 in solid state at room temperature [9]. This is the first time report on the photophysical properties of N-heterocyclic carbene copper complexes.

Surprisingly, studies on the luminescent properties of the four-coordinated NHC-Cu(I) complexes are very scarce. Wang and coworkers in 2016 reported the first study on the luminescence behavior of the four-coordinated NHC-Cu(I) complexes, in which the photoluminescence band maximum was found to be blue-shifted from 570 to 520 nm with high emission intensity [10].

These research results inspire us to continue the research of the Cu(I)-NHC. In this paper, we reported the synthesis and photophysical properties of a four-coordinate Cu(I)-NHC complex.

Experimental Section

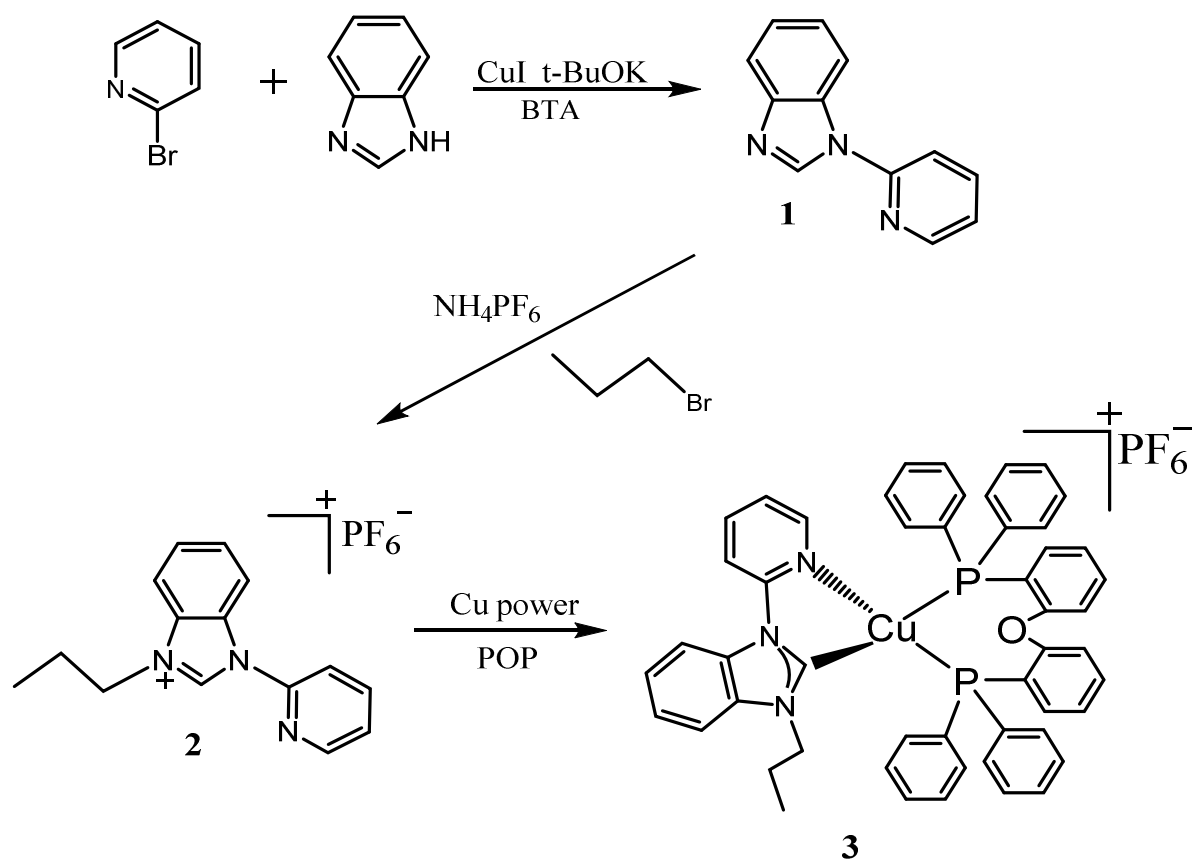
General. All the chemicals and solvents were obtained from commercial suppliers and used without further purification. ¹H NMR spectra were performed in an Bruker AV400MHz spectrometer, using tetramethylsilane (TMS) as internal reference. UV-vis absorption spectra were measured using a Perkin Elmer Lambda-900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

Synthesis of 1. A round-bottom flask containing benzimidazole (2.360 g, 20 mmol), 2-Bromopyridine (5.214 g, 33 mmol), KOtBu (2.464 g, 22 mmol), 1H-benzotriazole (0.238 g, 2 mmol), CuI (0.19 g, 1 mmol) and (20 mL) was stirred at 110 °C for 12 h under N₂. Cool water (100 mL) was added, and the mixture was extracted with dichloromethane, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness under reduced pressure. The product was purified by column chromatography (ethyl acetate/petroleum ether=3:1). The organic solution was evaporated with a rotary evaporator; a yellow oil was obtained (2.18 g, 56%). ¹H NMR

(400 MHz, DMSO) δ 8.98 (s, 1H), 9.65 (d, J = 4.7 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.09 (t, J = 7.8 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.78 (t, J = 9.4 Hz, 1H), 7.51–7.30 (m, 3H).

Synthesis of 2. A mixture of 1 (0.97 g, 5 mmol) and 1-bromopropane (0.62 g, 5 mmol) in 10 mL of toluene was refluxed for 1 d and cooled to room temperature. The solvent was filtered to remove the insoluble substances. The solid was dissolved in 50 mL water; then NH_4PF_6 (1.63 g, 10 mmol) was added and reacted for 1 h. The solvent was filtered and the precipitate removed under vacuum and obtain the white solid (1.55 g, 75%). ^1H NMR (400 MHz, DMSO) δ 10.49 (s, 1H), 8.79 (d, J = 4.2 Hz, 1H), 8.61–8.41 (m, 1H), 8.30 (t, J = 7.7 Hz, 1H), 8.26–8.20 (m, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.84–7.69 (m, 3H), 4.58 (t, J = 7.2 Hz, 2H), 2.21–1.91 (m, 2H), 1.01 (t, J = 7.3 Hz, 3H).

Synthesis of 3. A mixture of 2 (0.5 g, 1.2 mmol), bis[2-(diphenylphosphino)phenyl]ether (POP) (1 g, 1.8 mmol) and Cu (0.11 g, 1.7 mmol) in 15 mL of acetonitrile was stirred for 20 h at 50 °C. 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 washed with methanol; a light yellow was obtained (0.61 g, 47%). ^1H NMR (400 MHz, DMSO) δ 8.34 (d, J = 8.5 Hz, 2H), 8.19 (s, 1H), 8.09 (s, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.60–7.48 (m, 3H), 7.47–7.35 (m, 5H), 7.30 (d, J = 6.6 Hz, 6H), 7.20 (s, 6H), 7.09 (s, 5H), 6.95 (s, 4H), 6.65 (s, 2H), 3.97 (s, 2H), 1.32 (s, 2H), 0.46 (t, J = 7.1 Hz, 3H).



Results and Discussion

UV-Vis Spectra.

Fig.1 shows the absorption spectra of 2 in 1×10^{-4} mol/L CH_2Cl_2 solution and 3 in 2.5×10^{-5} mol/L CH_2Cl_2 solution at room temperature. At high energy region the complexes 3 shows intense absorption bands at 260–300 nm, which are quite similar to those of free ligands 2 and thus attributed to the $\pi \rightarrow \pi^*$ transitions of both NHC precursors and POP. In addition, at lower energy region the weak absorption band at 325 nm of 3, not observed in absorption spectra of the free ligands 2, can be tentatively assigned to metal-(Cu)-to-ligand charge-transfer (MLCT) transition.

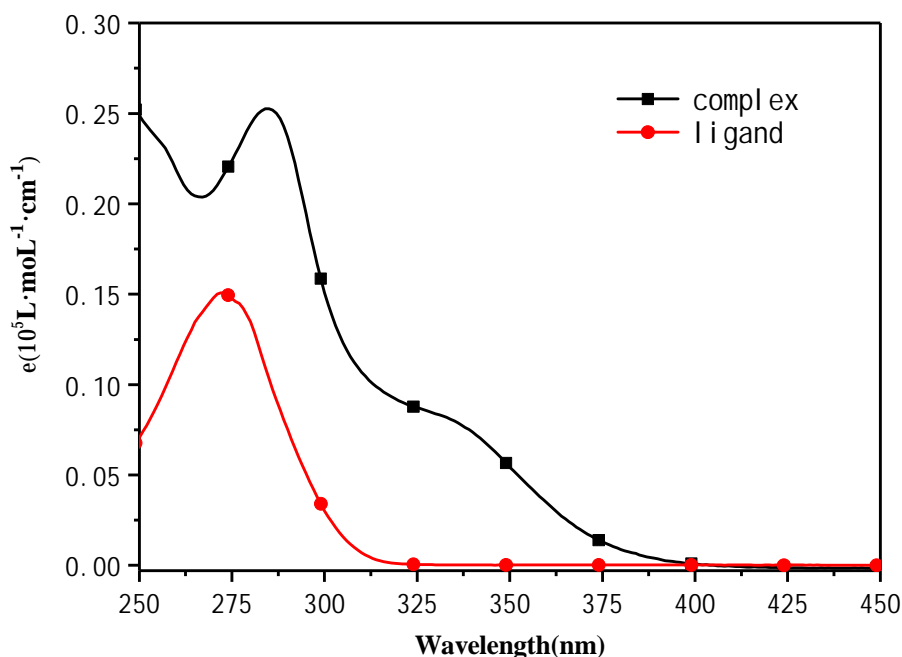


Figure 1. UV-vis absorption spectra of **2** in 1×10^{-4} mol/L CH_2Cl_2 solution and **3** in 2.5×10^{-5} mol/L CH_2Cl_2 solution at room temperature

Emission Spectra.

The emission spectrum of **3** were obtained at room temperature in PMMA film. As shown in Fig.2 and Fig.3, **3** exhibits broad and structureless emission peak at 552 nm and lifetime is 49.37 μs in PMMA film at room temperature; emission peak at 548 nm and lifetime is 78.42 μs in power state at room temperature. It suggested that this emission could be assigned to the triplet $^3\text{MLCT}$ character.

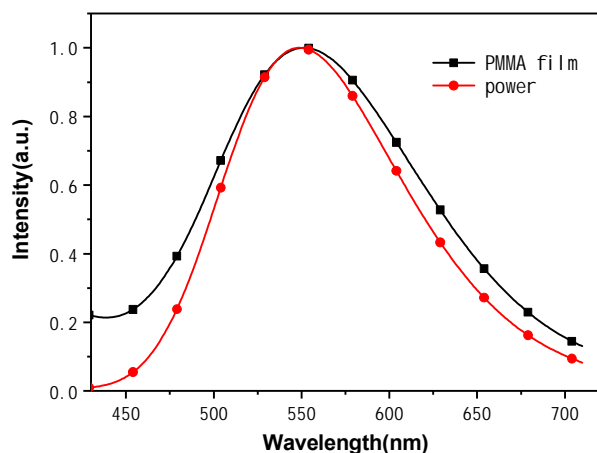


Figure 2. Emission spectra of **3** in the PMMA film and in power state at room temperature.

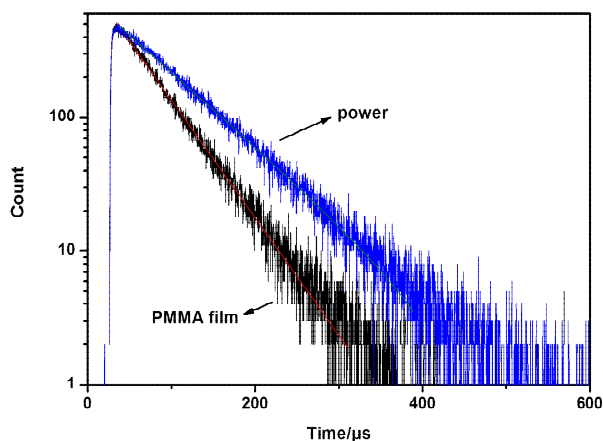


Figure 3. Excited-state lifetime of **3** in the PMMA film and in power state at room temperature

Conclusions

In this paper, a new four-coordinate NHC–Cu(I) complex, has been synthesized and characterized. The complex was obtained by addition of the NHC precursor to the mixture solution of Cu powder and POP ligand. It exhibits higher quantum yield and longer lifetime. The complex in PMMA film emission wavelength at 552 nm at room temperature and with quantum yields of 69.4% and lifetime of 49.37 μs . The complex exhibiting the yellow luminescence with the quantum yield of 100% and lifetime of 78.42 μs in power state at room temperature.

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