

## PREPARATION AND PROPERTIES OF THREE NEUTRAL COPPER (I) COMPLEXES BASED ON BIS[2- (DIPHENYLPHOSPHINO)PHENYL]ETHER) PHENYL] ETHER AND SUBSTITUTED IMIDAZOLE-2,9- DIMETHYL-1,10-PHENANTHROLINE

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**Abstract:** With deprotonated 2-(4-nitro phenyl)-, 2-(4-methyl phenyl)-, and 2-(4-methoxy phenyl) imidazoled-2,9-dimethyl-1,10-phenanthroline (NPIP, MPIP and MoPIP) as nitrogen ligands, as well as bis[2-(diphenylphosphino) phenyl]ether (DPEphos) as phosphorus ligand, three Cu(I) neutral complex has been synthesized and characterized by infrared spectroscopy (IR), elemental analysis and <sup>1</sup>H NMR methods. TG-DTA shows that the complex begins to decompose when the temperature reached about 220 °C, indicating their high thermo-stability. The emission spectrum shows that the complexes exhibit yellow emission with a peak emission wavelength of 576, 585 and 596 nm under excitation of 287 nm in powder state.

**Keywords:** *Cu (I) complex, luminescence, thermal stability, UV spectra*

## INTRODUCTION

The design and synthesis of copper (I) complexes have attracted considerable interests in recent decades because of their accessibility and less toxicity of raw materials and their perfect luminescent properties [1, 2]. 1, 10-phenanthroline (1, 10-phen) is an excellent ligand to construct luminescent transition metal complexes because it has extended  $\pi$ -system and rigid structure [3, 4]. However,  $[\text{Cu}(1,10\text{-phen})(\text{PPh}_3)_2]$  series are not emissive because their tetrahedral geometry may distort to square planar geometry and accelerate non-radiative decay of the excited-state [5, 6]. Introduction of substituent in the 2,9-positions of 1,10-phen can prevent the flattening distortion [7]. So far, copper (I) complexes containing 2,9-dialkyl-1,10-phen and phosphine auxiliary ligands have been widely used to construct of photo- and electroactive devices [8, 9]. However, such types of copper (I) complexes are primarily ionic complexes, more general copper (I) neutral complexes are rarely reported. A imidazole-1,10-phen ligand interest us because they combine the versatile structural properties of imidazole (labile proton) and 1,10-phen (extended  $\pi$ -system). Luminescent copper (I) neutral complexes can be prepared when the ligand is deprotonated in alkaline environment.

In this article, we report the syntheses and characterizations of three neutral copper(I) neutral complexes  $\text{Cu}(\text{NPIP})(\text{DPEphos})$  (**1**),  $\text{Cu}(\text{MPIP})(\text{DPEphos})$  (**2**) and  $\text{Cu}(\text{MoPIP})(\text{DPEphos})$  (**3**) containing deprotonated 2-(4-nitro phenyl)-, 2-(4-methyl phenyl)-, and 2-(4-methoxy phenyl) imidazole-2,9-dimethyl-1,10-phenanthroline, respectively, and bis [2-(diphenylphosphino)phenyl]ether) phenyl ] ether) (DPEphos) ancillary ligand. The thermal stability, absorption spectra and emission spectra of the complexes have also been studied.

## MATERIALS AND METHODS

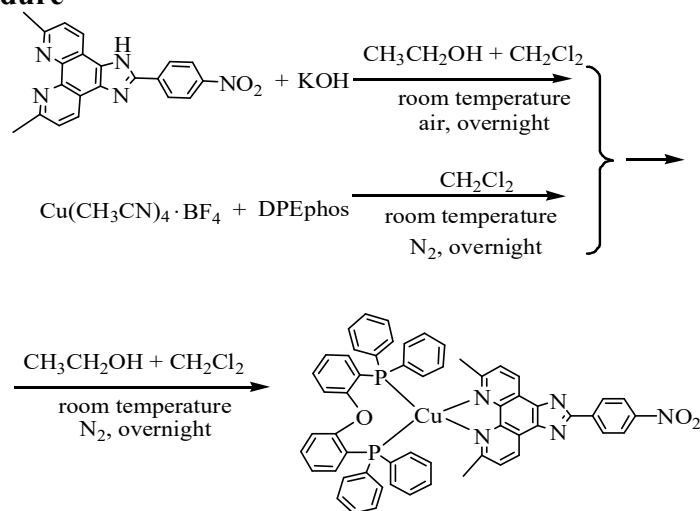
### Materials and characterization methods

Commercially available chemicals such as  $\text{CuCl}$ , DPEphos, 4-nitro benzaldehyde, 4-methyl benzaldehyde, 4-methoxy benzaldehyde, 1,10-phen monohydrate and fluoroboric acid ( $\text{HBF}_4$ ) are obtained from commercial sources and used as received. NHPiP, MHPiP and MoHPiP [10] and reaction precursor  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$  [11] are prepared according to the literature procedures with slight modification. All the solvents are purified by suitable methods and freshly distilled prior to use. All air sensitive manipulations are carried out under nitrogen using a standard schlenk flask.

$^1\text{H}$  NMR (400 MHz) is collected on a Bruker ACF-400 spectrometer and the NMR chemical shifts are recorded with deuterated DMSO as solvent. Elemental analyses (C, H, O and N) are determined using a Bio-Rad elemental analysis system. Absorption spectra are measured using a TU-1901 UV-Vis spectrophotometer. PL spectra are obtained using an RF-5301PC spectrofluorimeter connected to a photomultiplier tube with a xenon lamp as the excitation source.

The preparation of complex **1** is outlined in Scheme 1 as a representative to clearly show the preparation process.

## Synthesis procedure



**Scheme 1.** Preparation of  $\text{Cu}(\text{NPIP})(\text{DPEphos})$  (**1**)

$\text{Cu}(\text{NPIP})(\text{DPEphos})$  (**1**): A mixture of  $\text{Cu}(\text{CH}_3\text{CN})_4 \cdot \text{BF}_4$  (0.064 g, 0.2 mmol) and DPEphos (0.108 g, 0.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was stirred in a Schlenk flask under nitrogen for 5 hours. Meanwhile a  $\text{CH}_2\text{Cl}_2$  (10 mL) and  $\text{CH}_3\text{CH}_2\text{OH}$  (10 mL) mixture of NPIP (0.074 g, 0.2 mmol) and KOH (0.012 g, 0.2 mmol) was stirred in a round-bottomed flask to give a yellow solution, which was then transferred to the Schlenk flask by a syringe. The resulting mixture was stirred under nitrogen for 72 hours at 35 °C. The solvents were removed and the residue was dissolved in diethyl ether. Yellow tiny crystals were obtained after standing overnight (0.147 g, 78 %). IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3054 w, 2357 w, 1964 w, 1817 w, 1593 m, 1553 w, 1515 m, 1479 w, 1434 m, 1338 s, 1259 w, 1179 w, 1093 m, 1059 s, 997 m, 925 w, 852 m, 741 s.  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta$  8.86 (d,  $J = 71.1$  Hz, 2H), 8.54 (d,  $J = 67.7$  Hz, 2H), 8.31 - 7.96 (m, 2H), 7.81 - 7.42 (m, 6H), 7.41 - 7.27 (m, 8H), 7.17 (s, 4H), 7.07 (d,  $J = 7.8$  Hz, 6H), 6.98 - 6.64 (m, 6H), 2.53 (dd,  $J = 26.5, 19.5$  Hz, 6H). Anal. Calcd for  $\text{C}_{57}\text{H}_{42}\text{CuN}_5\text{O}_3\text{P}_2$ : C, 70.55 %; H, 4.36 %; N, 7.22 %. Found: C, 70.92 %; H, 4.43 %; N, 7.59 %.

$\text{Cu}(\text{MPIP})(\text{DPEphos})$  (**2**): synthesized in the same way as **1**. Yield: 75%. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3060 m, 1688 w, 1644 w, 1571 m, 1507 m, 1442 s, 1390 w, 1348 m, 1311 w, 1263 w, 1215 m, 1104 w, 1034 w, 803 m, 740 s, 697 s.  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta$  9.08 (s, 2H), 8.33 (s, 2H), 7.71 - 7.54 (m, 4H), 7.42 - 7.32 (m, 8H), 7.29 - 7.25 (m, 10H), 7.18 - 7.02 (m, 10H), 2.56 (s, 6H), 2.34 (s, 3H). Calcd for  $\text{C}_{58}\text{H}_{45}\text{CuN}_4\text{OP}_2$ : C, 74.25; H, 4.83; N, 5.97 %. Found: C, 74.65 %; H, 4.95 %; N, 6.28 %.

$\text{Cu}(\text{MPIP})(\text{DPEphos})$  (**3**): synthesized in the same way as **1**. Yield: 82 %. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3056 w, 2338 w, 1965 w, 1819 w, 1609 m, 1585 m, 1563 w, 1511 m, 1480 m, 1460 m, 1434 m, 1347 m, 1295 w, 1247 m, 1214, 1173 m, 1093 m, 1059 s, 1024 s, 998 m, 957 m, 874 m, 831 m, 800 m, 741 s, 693 s, 669 s.  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta$  8.93 (d,  $J = 38.4$  Hz, 2H), 8.16 (s, 2H), 7.64 (d,  $J = 50.7$  Hz, 4H), 7.45 (d,  $J = 7.2$  Hz, 2H), 7.37 (d,  $J = 11.9$  Hz, 4H), 7.32 - 7.14 (m, 8H), 7.08 (d,  $J = 8.0$  Hz, 4H), 6.96 (s, 6H), 6.72 (d,  $J = 50.3$  Hz, 4H), 3.56 (s, 3H), 2.52 (s, 6H). Calcd for  $\text{C}_{58}\text{H}_{45}\text{CuN}_4\text{O}_2\text{P}_2$ : C, 73.00; H, 4.75; N, 5.87 %. Found: C, 73.32; H, 4.91; N, 6.12 %.

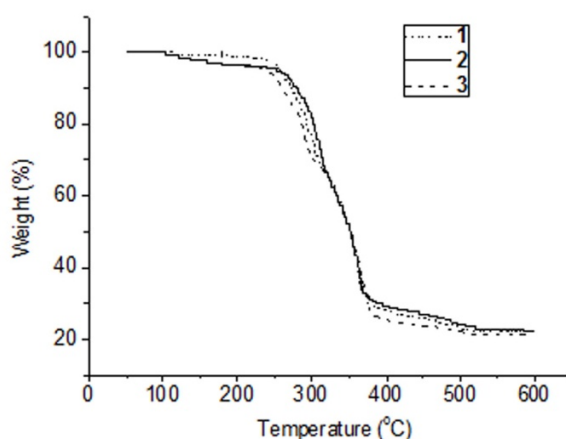
## RESULTS AND DISCUSSION

### Syntheses and characterization

KOH was preferentially encouraged to react with N-donor ligand to form NPIP anion, and then added into the mixture of  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$  and  $\text{PPh}_3$ . That is, the side reaction of KOH with  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$  is prevented in advance. During the deprotonation of nitrogen ligand, KOH is proven to be a better candidate compared with NaOH because  $\text{K}^+$  matches well with  $\text{BF}_4^-$  in radius.

In the  $^1\text{H}$  NMR spectra of **1**, **2** and **3**, the C-H signals of the methyl group at 2,9-positions of 1,10-phen are observed at 2.53, 2.56 and 2.52 ppm, respectively. The C-H signals of the methyl (**2**) and methoxy (**3**) group at para-position of benzimidazole are observed at 2.34 and 3.56 ppm, respectively. The aromatic proton signals are observed at 6.64-8.86, 7.02-9.08 and 6.72-8.93 ppm for **1**, **2** and **3**, respectively. The numbers and positions of proton signals confirm the simultaneous coordination of N- and P-donor ligand. Furthermore, the vanishing of N-H signal of the imidazole ring at around 14 ppm confirms the deprotonation of the N-donor ligand.

### Thermal properties



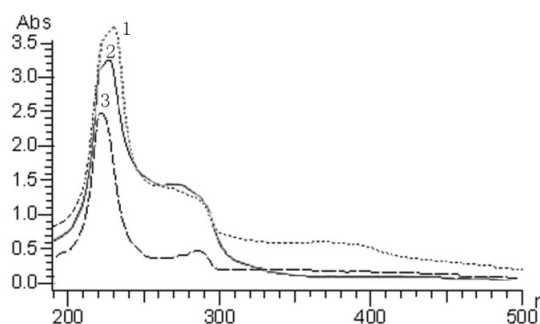
**Figure 1.** TG curves of the complexes

In order to determine the thermal stabilities of the complexes, pyrolysis experiments were carried out by means of TG and the thermal curves were illustrated in Figure 1. Complexes **1**, **2** and **3** are stable from 30 to about 230 °C indicating their good thermal stability. From 230 to 400 °C, there is an obvious thermal decomposition process corresponding to the gradual decomposition of organic ligands. In conclusion, the complexes are thermally stable enough to meet the needs of actual applications in many fields.

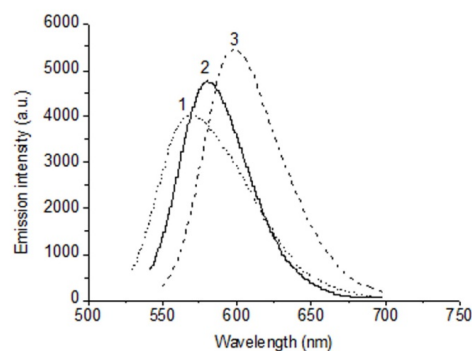
### Absorption spectra

The UV-Vis absorptions of the complexes in anhydrous ether are shown in Figure 2. Complexes **1**, **2** and **3** all show an intense absorption peak at about 228 nm, and a weak shoulder peak at about 287 nm. According to the literature [12], the high-energy

absorptions below 300 nm are ascribed to the ligand transitions ligand-to-ligand charge transfer (LLCT) and intraligand charge transition (ILCT). However, the low energy absorption bands above 300 nm which have been identified as the metal-to-ligand charge-transfer (MLCT) by reported literature [12] are obscure and nearly invisible.



**Figure 2.** Absorbance spectra of the complexes in anhydrous ether



**Figure 3.** Emission spectra of the complexes in powder state

### Emission spectra

Emission spectra are measured at room temperature in different solvent under excitation of 287 nm. They are not emissive in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{OH}$  and anhydrous  $\text{CH}_3\text{CN}$ . However, moderate green (1) to yellow (2 and 3) luminescence ( $\lambda_{\text{max}} = 572, 582$  and  $593$  nm for **1**, **2** and **3**, respectively) is observed in anhydrous ether. According to the literatures, the tendency of the emission energies ( $\mathbf{1} > \mathbf{2} > \mathbf{3}$ ) is contrary to the electron-donating ability of the N-donor ligand ( $\text{NPIP} < \text{MPIP} < \text{MoPIP}$ ) [13]. For emission spectra in solid-powder states (Figure 3), the three complexes exhibit strong emission intensity and similar emission ( $\lambda_{\text{max}} = 576, 585$  and  $597$  nm for **1**, **2** and **3**, respectively) with the solution emissions. The emission wavelength of **3** (597 nm) is more red-shifted than that of **2** (585 nm). The red-shift may be caused by the introduction of the electron-donating methyl group in the N-donor ligand, raising the LUMO level, less influencing the HOMO energy, thus decreasing the HOMO-LUMO gap [14].

### CONCLUSION

We have synthesized three neutral mononuclear Cu(I) complexes bearing three different 1,10-phen-imidazole ligand and DPEphos. This paper describes the thermal stability, absorption spectra and emission spectra of the complexes at ambient temperature.

### ACKNOWLEDGMENTS

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