Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Characterization of Copper(I) Complexes with Triazole Derivative Ligands Containing an α-Diimine Moiety

Wen-Jwu Wang [a], Chien-Ho Lin [a], Jau-Shuenn Wang [a] & Shang-Wei Tang [a]

[a] Department of Chemistry, Tamkang University, Tamsui, Taipei, Taiwan (ROC)

Version of record first published: 21 Dec 2006

To cite this article: Wen-Jwu Wang, Chien-Ho Lin, Jau-Shuenn Wang & Shang-Wei Tang (2006): Synthesis and Characterization of Copper(I) Complexes with Triazole Derivative Ligands Containing an α-Diimine Moiety, Molecular Crystals and Liquid Crystals, 456:1, 209-219

To link to this article: http://dx.doi.org/10.1080/15421400600788740

Mol. Cryst. Liq. Cryst., Vol. 456, pp. 209–219, 2006

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600788740

Taylor & Francis
Taylor & Francis Group

Synthesis and Characterization of Copper(I) Complexes with Triazole Derivative Ligands Containing an α-Diimine Moiety

Wen-Jwu Wang
Chien-Ho Lin
Jau-Shuenn Wang
Shang-Wei Tang
Department of Chemistry, Tamkang University, Tamsui, Taipei, Taiwan (ROC)

*Two cuprous complexes Cu(L1)(PPh$_3$)I (**1**) and Cu(L2)(PPh$_3$)I (**2**) were obtained by reaction of Cu(PPh$_3$)$_3$I (PPh$_3$ = triphenylphosphine) with two different α-diimine ligands* $\mathbf{L_1}$*(3,5-di(2′-pyridyl)-4-amino-1,2,4-triazole) and* $\mathbf{L_2}$ *(N-benzylidene-3,5-di (2′-pyridyl)-4-amino-1,2,4-triazole, respectively. These two complexes have been characterized by UV-Vis, luminescence,* ^{1}*H NMR spectroscopy and cyclic voltammetric studies. The structures are confirmed by the single crystal X-ray diffraction study. The compound Cu(L1)(PPh$_3$)I (**1**) crystallizes in the triclinic space group P-1 with* $a = 8.3188(14)$, $b = 9.2243(15)$, $c = 21.177(4)$, $\alpha = 78.156(3)$, $\beta = 86.45(3)$, $\gamma = 65.966(3)$, $Z = 2$ *and the compound Cu(L2)(PPh$_3$)I (**2**) crystallizes in the triclinic space group P-1 with* $a = 8.9671(7)$, $b = 13.9737(11)$, $c = 14.6850(12)$, $\alpha = 82.2580(10)$, $\beta = 75.7020(10)$, $\gamma = 72.2790(10)$, $Z = 2$. *Both complexes show an MLCT band at* $340 \sim 545$ *nm region and complex* **2** *exhibits luminescence at room temperature in a dichloromethane solution. The cyclic voltammogram of Cu(L1)(PPh$_3$)I shows the redox couples at* $+0.36$ *and* -0.545 *V.*

Keywords: α-diimine ligands; luminescence; triazole; X-ray

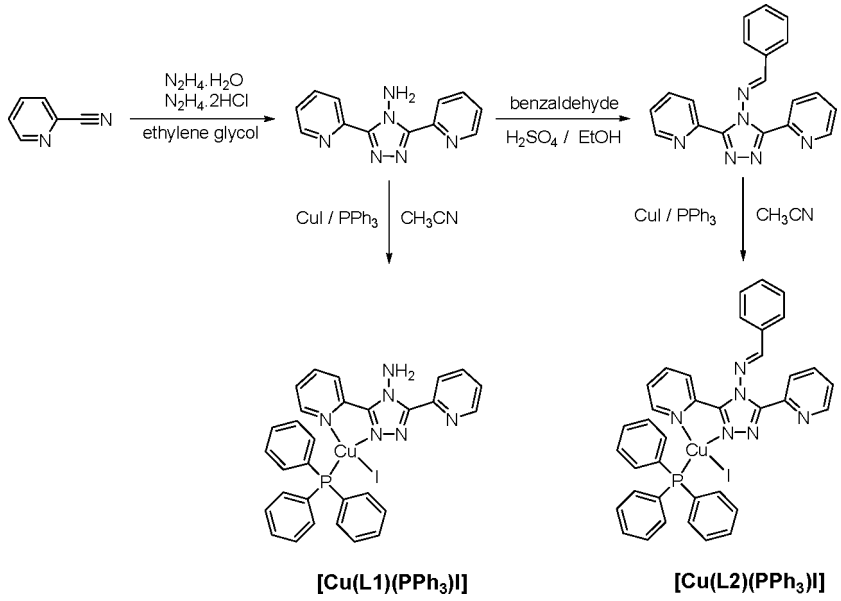
INTRODUCTION

It is known that mixed ligand Cu(I) complexes exhibit unusually efficient [1–6], long-lived photoluminescence signals because of the

This work was supported by the National Science Council of Taiwan (ROC) and Tamkang University.

Address correspondence to Wen-Jwu Wang, Department of Chemistry, Tamkang University, Tamsui 25137, Taipei, Taiwan (ROC). E-mail: wjw@mail.tku.edu.tw

lowest energy (charge-transfer) state of d^{10} system, which involves excitation from a metal to ligand ($d\pi^*$) orbital [7]. Moreover, their rather flexible coordination geometry and strong bonding to pyridine-donors have contributed to their widespread application. For example, Cu(I) complexes, including those with aromatic α-diimine ligands, have been widely studied with regard to luminescence [8–15]. Recently, Wang and co-workers have been demonstrated phosphorescent Cu(I) complexes to be promising phosphorescent emitters in OLEDs [16]. This prompted us to undertake a programme in the development of new phosphorescent Cu(I) compounds. The previously reported Cu(I) complexes are mononuclear green emitters that contain a phenanthroline N,N-chelate (or a derivative) and two phosphine donors, which have been shown by McMillin and co-workers to play a key role in stabilizing the Cu(I) center [5,17]. In our laboratory, we have synthesized two new Cu(I) complexes based on 3,5-di(2′-pyridyl)-4-amino-1,2,4-triazole and a derivative ligand (Scheme 1). Herein, we report the syntheses, structural characterization, luminescent and electrochemical properties of Cu(L1)(PPh_3)I and Cu(L2)(PPh_3)I.



SCHEME 1 Synthesis of Ligands and complexes.

EXPERIMENTAL

Synthesis of Ligands and Complexes

3,5-Di(2′-pyridyl)-4-amino-1,2,4-triazole [18] (L1)

A mixture of 2-cyanopyridine (10.4 g, 0.1 mol), hydrazine dihydrochloride (10.5 g, 0.1 mol) and hydrazine hydrate (15 g, 0.3 mol) in ethylene glycol (50 mL) were heated at 130°C for 6 hr. After cooling the reaction mixture was diluted with water (200 mL). The precipitate thus obtained was filtered, washed with water, dried and recrystallized from ethanol as a white powder. The yield was 10.1 g (85%). ^{1}H-NMR (300 MHz, CD_3CN) δ(ppm), J (Hz): 8.7 (d, 2H, bi-py-H, $J = 4.6$), 8.26 (d, 2H, bi-py-H, $J = 8.1$), 8.13 (s, 1H, -NH), 7.96 (t, 2H, bi-py-H, $J = 7.8$), 7.46 (t, 2H, bi-py-H, $J = 6.2$).

N-benzylidene-3,5-Di(2′-pyridyl)-4-amino-1,2,4-triazole) [19] (L2)

The ligand L1 (8 g, 33.6 mmol), benzaldehyde (14.25 g, 34.4 mmol) and two drops of concentrated H_2SO_4 were dissolved in absolute ethanol (40 mL) and heated to reflux for 5 hr under a N_2 atmosphere. After cooling the solution and on evaporation, the product was obtained as an oil, which was precipitated by addition of 10 mL ether. The resulting solid was filtered, washed with ether, dried and recrystallized from ethanol as white powder. The yield was 8.8 g (80%).^{1}H-NMR (300 MHz, CD_3CN) δ(ppm), J (Hz): 8.75(s, 1H, $-$HC=N), 8.53 (d, 2H, bi-py-H, $J = 5.3$), 8.12 (d, 2H, bi-py-H, $J = 8.3$), 7.91 (t, 2H, bi-py-H, $J = 8.7$), 7.76 (d, 2H, Ar-H, $J = 7.3$), 7.60 (t, 1H, Ar-H, $J = 3.6$), 7.52 (t, 1H, Ar-H, $J = 7.4$), 7.40 (t, 2H, bi-py-H, $J = 6.2$). Anal. calcd for $C_{19}H_{14}N_6$: C, 69.92; H, 4.32; N, 25.75. Found: C, 69.74; H, 4.36; N, 25.77.

Cu(L1)(PPh$_3$)I (1)

Copper(I) iodide (95 mg, 0.5 mmol) dissolved in CH_3CN (15 mL) was added slowly to an acetonitrile solution (15 mL) of triphenylphosphine (PPh_3, 400 mg, 1.5 mmol). The mixture was stirred for 10 min at room temperature. Then **L1** (119 mg, 0.5 mmol) dissolved in CH_3CN (15 mL) was added slowly into the $Cu(PPh_3)_3I$ solution. The color of the resulting solution appeared as light yellow. The solution was then stirred for 30 mins at room temperature to complete the reaction and the yellow oil obtained on evaporation was precipitated by the addition of ether (10 mL). The resulting was filtered, washed with ether, dried and recrystallized from acetonitrile. The yellow crystals were separated. The yield was 252 mg (73%). ^{1}H-NMR (300 MHz, CD_3CN) δ (ppm),

J (Hz): 8.67 (d, 2H, bi-py-H, $J = 4.6$), 8.39 (d, 2H, bi-py-H, $J = 4.6$), 7.99 (t, 2H, bi-py-H, $J = 8.2$), 7.48 (t, 2H, bi-py-H, $J = 6.5$), 7.39 (m, 17H, Ar-H). Anal. calcd for $C_{30}H_{25}CuIN_6P$: C, 52.15; H, 3.65; N, 12.16. Found: C, 52.32; H, 3.68; N, 11.95.

Cu(L2)(PPh$_3$)I (2)

The compound Cu(L2)(PPh_3)I was obtained by the same procedure as describe above. Yield of the yellow crystal after recrystallization from CH_3CN in a 75% yield. ^{1}H-NMR (300 MHz, CD_3CN) δ (ppm), J (Hz): 8.72 (s, 1H, −HC=N), 8.54 (d, 2H, bi-py-H, $J = 5.3$), 8.22 (d, 2H, bi-py-H, $J = 7.8$), 7.96 (t, 2H, bi-py-H, $J = 8.0$), 7.89 (d, 2H, Ar-H, $J = 8.1$), 7.67 (t, 1H, Ar-H, $J = 7.5$), 7.56 (t, 2H, Ar-H, $J = 7.5$), 7.38 (m, 14H, Ar-H and 2H, bi-py-H). Anal. calcd for $C_{37}H_{29}CuIN_6P$: C, 57.04; H, 3.75; N, 10.79. Found: C, 57.19; H, 3.77; N, 10.84.

RESULTS AND DISCUSSION

Ligand and Complexes

The ligands **L1** and **L2** are excellent bidentate chelators which bind to Cu(I) ions. The reactions of these ligands with the stoichiometric amount of $Cu(PPh_3)_3I$ resulted in good yields of the corresponding yellow crystals of Cu(I) complexes, Cu(L1)(PPh_3)I (**1**) and Cu(L2)(PPh_3)I (**2**), respectively. At the time of recrystallization, we obtained the X-ray quality single crystals, which are stable in solution under air. The structures of these complexes were therefore determined by single-crystal X-ray diffraction analysis.

Molecular Structure

Crystal data are listed in Table 1 and selected bond parameters are summarized in Table 2. The molecular structures of compounds **1** and **2** are shown in Figure 1. Compound **1** and **2** belong to the triclinic space group P-1. The Cu(I) ion of these compounds have a distorted tetrahedral geometry with one PPh_3, one I^- and one diimine ligand. There is a significant difference between the two Cu-N bond lengths. In both cases, it was observed that Cu-N(pyridyl) bond length is longer than that of Cu-N(triazole) bond length: (Cu(1)-N(1) (pyridyl) 2.145(4) Å; Cu(1)-N(2) (triazole, 2.050(4) Å for **1** and, Cu(1)-N(6) (pyridyl), 2.1369(19) Å; Cu(1)-N(4) (triazole, 2.1028(19) Å for **2**). This indicates that the triazole nitrogen atom is a stronger donor than that of the pyridyl nitrogen.

TABLE 1 Crystal Data and Structure Refinement for Cu(L1)(PPh_3)I and Cu(L2)(PPh_3)I

Parameter	Cu(L1)(PPh_3)I	Cu(L2)(PPh_3)I
Formula	C_{30} H_{25} Cu I N_6 P	C_{37} H_{29} Cu I N_6 P
Mw	690.97	779.07
T/K	298(2)	298(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Tricilinic	Tricilinic
Space group	P-1	P-1
a(Å)	8.3188(14)	8.9671(7)
b(Å)	9.2243(15)	13.9737(11)
c(Å)	21.177(4)	14.685(12) Å
α (deg)	78.156(3)	82.2580(10)
β(deg)	86.450(3)	75.702(10)
γ(deg)	65.966(3)	72.279(10)
V(Å^3)	1452.1(4)	1694.9(2) Å^3
Z	2	2
D_{calc}, g cm^{-3}	1.580	1.527
μ, cm^{-1}	1.900	1.638
Θ, deg	0.98 to 28.34	2.03 to 28.34
F(000)	688	780
Limiting indices	$-10 \le h \le 10$, $-12 \le k \le 11$, $-27 \le l \le 27$	$-11 \le h \le 11$, $-18 \le k \le 18$, $-19 \le l \le 19$
Reflcns collcd/unique/R_{int}	17435/6904/0.0351	2024/8029/0.0205
Completeness to theta = 28.28	95.2%	95.1%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restr/params	6904/0/352	8029/0/415
GOF on F^2	1.059	1.043
Final [$I > 2\ \sigma$(I)]		
R_1	0.0553	0.0338
wR_2	0.1258	0.0768
R (all data)		
R_1	0.0844	0.0420
wR_2	0.1440	0.0804
Largest diff. peak and hole (e. Å^{-3})	0.807 and −0.600	0.729 and −0.228

^{1}H NMR Spectra

The ^{1}H-NMR spectra of compounds **1** and **2** at 298 K are shown in Figure 2. The spectra display only one set of chemical shifts, which does not conform to the asymmetric structure of the compounds in the solid state as established by their crystal structure. Wang and co-worker have studied the variable temperature (298 to 203 K) ^{1}H-NMR spectra of [HB(7-aza)$_3$](Cu(PPh_3)) (7-aza = 7-azaindolyl)

TABLE 2 Selected Bond Distances (Å) and Angles (°)

$Cu(L1)(PPh_3)I$			
Cu(1)-N(1)	2.145(4)	N(2)-Cu(1)-N(1)	78.16(14)
Cu(1)-N(2)	2.050(4)	N(2)-Cu(1)-P(1)	112.43(11)
Cu(1)-P(1)	2.1981(12)	N(1)-Cu(1)-P(1)	114.97(10)
Cu(1)-I(1)	2.5746(7)	N(1)-Cu(1)-I(1)	113.60(11)
		N(1)-Cu(1)-I(1)	106.25(10)
		P(1)-Cu(1)-I(I)	122.70(14)
$Cu(L2)(PPh_3)I$			
Cu(1)-N(4)	2.1028(18)	N(4)-Cu(1)-N(6)	77.55(7)
Cu(1)-N(6)	2.1369(19)	N(4)-Cu(1)-P(1)	124.15(6)
Cu(1)-P(1)	2.1984(6)	N(6)-Cu(1)-P(1)	115.22(6)
Cu(1)-I(1)	2.6155(4)	N(4)-Cu(1)-I(1)	100.90(6)
		N(1)-Cu(1)-I(1)	103.82(5)
		P(1)-Cu(1)-I(I)	124.51(19)

complex [20]. As the temperature is lowered gradually, all peaks become broad. At 233 K, each of the 7-azaindolyl peaks is resolved into two peaks with 1:2 ratio. This is consistent with the presence of a dynamic exchange process between the two coordinated 7-azaindolyl groups, and the non-coordinated 7-azaindolyl group. Hence, this led us to believe that the seemingly symmetric structure based on NMR data at room temperature for compounds **1** and **2** is most likely a consequence of dynamic exchange.

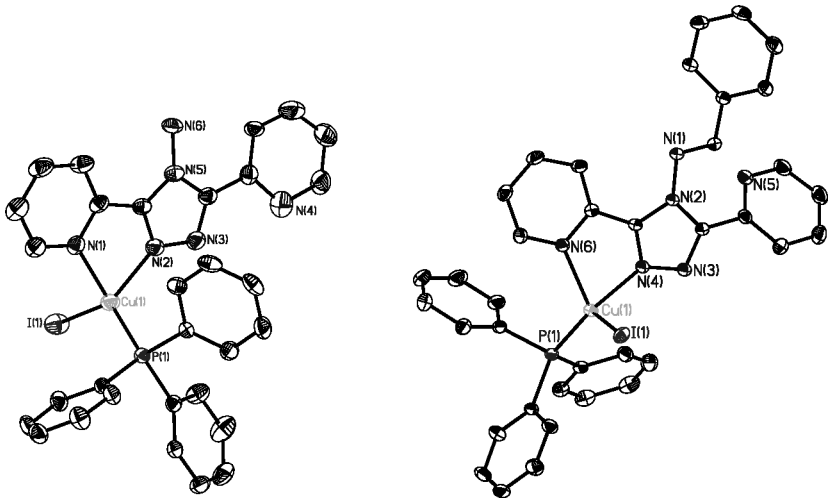


FIGURE 1 Crystal structure of Cu(L1)(PPh3)I and Cu(L2)(PPh3)I.

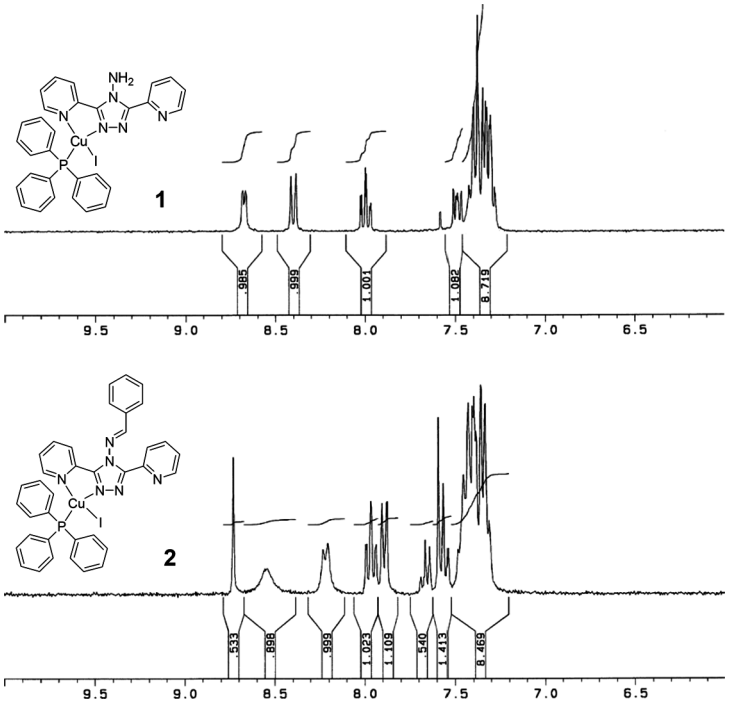


FIGURE 2 ^{1}H-NMR spectrum of **1** (up) and **2** (bottom) in CD_3CN.

Spectroscopic and Electrochemical Properties

The absorption spectra of the free ligands **L1**, and **L2** have two absorption bands at λ_{max} value 255 ($\varepsilon = 1.4 \times 10^4$ $M^{-1}cm^{-1}$) and 295 nm ($\varepsilon = 2.5 \times 10^4$ $M^{-1}cm^{-1}$) attributed to the intraligand (π-π^*) transition. In CH_2Cl_2, the absorption spectra of complex **2** has similar features as the ligands (Fig. 3).

In addition to the high energy absorption bands, complex **2** shows a weak and broad low-energy shoulder in the 340–545 nm region, which accounts for the yellow color of the complex. The same trend was also observed for the absorption spectra of complex **1**, due to the low-energy transition involving the low-lying unoccupied π^* orbital in N,N-chelate ligand and the electron-rich Cu(I) ion. In addition, this low-energy transition band resembles the MLCT band observed in [Cu(Phen)-$(PPh_3)_2$]BF_4 [5,17]. The MLCT bands of **1** and **2** shift towards a shorter wavelength in the polar solvent CH_3CN, as show in Figure 3, which is consistent with the behavior of related Cu(I) phenanthroline complexes.

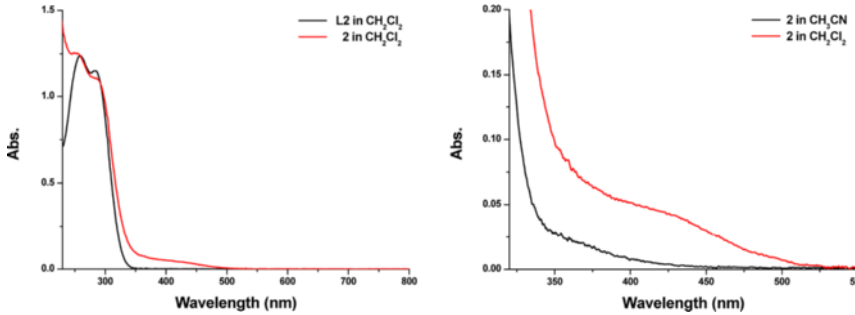


FIGURE 3 UV/Vis spectrum of L2, 2 in 5×10^{-5} M CH_2Cl_2 (left), and 2 in 5×10^{-5} M CH_2Cl_2, CH_3CN (right).

When irradiated by UV light, the free ligands emit a weak blue color with λ_{max} 310–420 nm in CH_2Cl_2 solution at ambient temperature. This band is assigned to fluorescence emission originating from a ligand-centered π-π^* transition. In contrast to the behavior of the free ligands, complex **2** displays a weak yellow emission with $\lambda_{max} = 636$ nm in CH_2Cl_2 solution at ambient temperature (Fig. 4). The excitation spectra for complex **2** confirms the presence of two absorption bands at about 375 and 480 nm, which is confirmed by the absorption spectra of **2** with an MLCT band at (340 $\sim$ 545 nm). The phosphorescence of

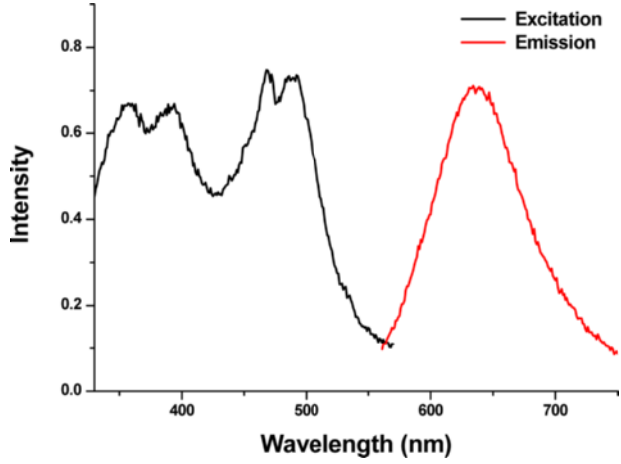


FIGURE 4 Emission (dashed line) and excitation (solid line) spectrum of 2 in 5×10^{-5} M CH_2Cl_2.

$[Cu(Phen)(PPh_3)_2]BF_4$ [5,17] was studied by McMillin and co-workers and at a lower temperature (77 K) they observed an emission decay time of 0.22 μs. Hence, we suggest that the emission of complex **2** maybe due to phosphorescence.

The redox properties of ligands and complexes were examined by cyclic voltammetry using a glassy carbon as working electrode in CH_3CN solution and in the presence of $TBAPF_6$ as a supporting electrolyte. The potentials are expressed with reference to the silver-silver chloride electrode (RE). The cyclic voltammogram of ligand **L1** shows two redox couples, one is negative to RE ($[L1]/[L1^-]$ at $E_{pc} = -1.97$ V) and other is positive to RE ($[L1]/[L1^+]$, at $E_{pa} = +1.37$ V). As the triazole ring contains three N atoms and is more electron rich than that of pyridine, which contains one N atom, the former corresponds to the irreversible reduction of pyridine/pyridine$^-$, and the latter to the irreversible oxidation of triazole/triazole$^+$. On comparing the redox behavior of the free ligand, complex **1** exhibits $[\mathbf{1}]/[\mathbf{1}^-]$, $[\mathbf{1}^-]/[\mathbf{1}^{2-}]$, $[\mathbf{1}]/[\mathbf{1}^+]$ and $[\mathbf{1}^+]/[\mathbf{1}^{2+}]$, at $E = -0.545$ V, $E_{pc} = -1.60$ V, $E = +0.36$ V, $E = +0.685$ V, respectively, vs. RE in CH_3CN solution at ambient temperature (Fig. 5). In a study by Zacharias and Masood, the redox behavior of the Cu(I) center in $[Cu(phen)_2]^+$ [21] showed the stripping peak of Cu(I)/Cu(0) at $E_{pc} = -0.62$ V vs. SCE in CH_3CN. This behavior is due to the absence of bulky groups at 2,9-position of *o*-phenanthroline, so that the complex $[Cu(phen)_2]^+$

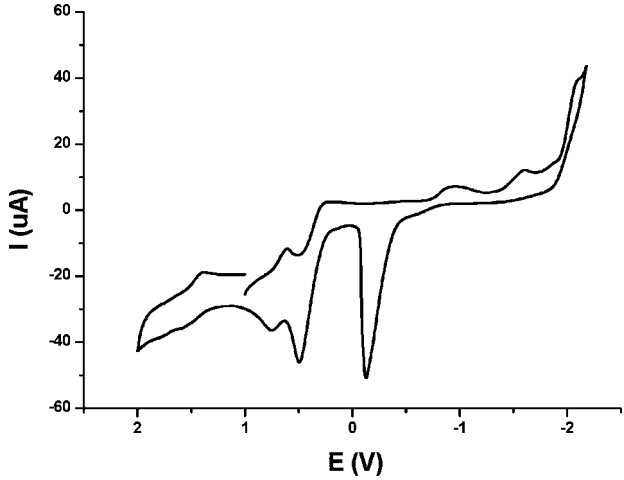


FIGURE 5 Cyclic voltammogram of **1** in CH_3CN solution (0.01 M $TBAPF_6$, glassy carbon electrode, 100 mV/s scan rate, current range 100 uA).

easily decomposes to Cu(0) and free ligand. At the same time, they observed the redox couple of Cu(I)/Cu(II) at $E = +0.6$ V. In our system, we also observed a stripping peak at $E_{pc} = -0.13$ V in the reduction region and a reversible couple at $E = +0.685$ V in the oxidation region. Hence, the former corresponds to the reduction of Cu(I)/Cu(0), and the latter is the reversible oxidation of Cu(I)/Cu(II). In contrast to the triphenylphosphineanalogue complexes [22], the redox behavior of PPh_3 at $E_{pc} = -1.60$ V undergoes irreversible reduction. Finally, we determined the irreversible redox couple of I^-/I_3^- at $E = +0.36$ V in the oxidation region, in agreement with the redox behavior of I^- from CuI at $E = +0.36$ V.

CONCLUSIONS

We have synthesized the diimine ligands benzylidene-3,5-Di(2′-pyridyl)-4-amino-1,2,4-triazole (**L1**) and N-benzylidene-3,5-Di(2′-pyridyl)-4-amino-1,2,4-triazole (**L2**) which were used to prepare complexes **1** and **2** with $Cu(PPh_3)_3I$. The two copper complexes were structurally characterized by X-ray and ^{1}H-NMR methods. The absorption spectra of complexes **1** and **2** showed an MLCT bond in the region of 345–545 nm. We have also measured the emission properties of complex **2** which was shown to have a $\lambda_{max} = 636$ nm. Cyclic valtammogram of complex **1** showed the redox couples of the copper center at $E = -0.545$ V and $E = +0.685$ V, the former corresponds to the reduction of Cu(I)/Cu(0), and the latter corresponds to the reversible oxidation of Cu(I)/Cu(II).

REFERENCES

[1] Vogler, C., Hausen, H.-H., Kaim, W., Kohlmann, S., Kramerm, H. E. A., & Rieker, J. (1989). *Angew. Chem., Int. Ed. Engl.*, *28*, 1659.
[2] Casadonte, D. J. & McMillin, D. R. (1987). *Inorg. Chem.*, *26*, 3950.
[3] Sieger, M., Vogler, C., Klein, A., Knodler, A., Wanner, M., Fiedler, J., Zalis, S., Snoeck, T. L., & Kalm, W. (2005). *Inorg. Chem.*, *44*, 4637.
[4] Tsubomura, T., Enoto, S., Endo, S., Tamane, T., Matsumoto, K., & Tsukuda, T. (2005). *Inorg. Chem.*, *44*, 6373.
[5] Cuttell, D. G., Kuang, S. M., Fanwick, P. E., McMillin, D. R., & Walton, R. A. (2002). *J. Am. Chem. Soc.*, *124*(1), 6.
[6] Jia, W. L., McCormick, T., Tao, Y., Lu, J. P., & Wang, S. (2005). *Inorg. Chem.*, *44*, 5706.
[7] McMillin, D. R. & McNett, K. M. (1998). *Chem. Rev.*, *98*, 1201.
[8] Dias, H. V. R., Diyabalanage, H. V. K., Rawasheh-Omary, M. A., Franzman, M. A., & Omary, M. A. (2003). *J. Am. Chem. Soc.*, *125*, 12072.
[9] Omary, M. A., Rawashdeh-Omary, M. A., Diyabalanage, H. V. K., & Dias, H. V. R. (2003). *Inorg. Chem.*, *42*, 8612.

[10] Riesgo, E. C., Hu, Y.-Z., Bouvier, F., Thummel, R. P., Scaltrito, D. V., & Meyer, G. J. (2001). *Inorg. Chem.*, *40*, 3413.
[11] Williams, R. M., De Cola, L., Hartl, F., Lagref, J.-J., Planeix, J.-M., De Cian, A., & Hosseini, M. W. (2002). *Coord. Chem. Rev.*, *230*, 253.
[12] Che, C.-M., Mao, Z., Miskowski, V. M., Tse, M.-C., Chan, C.-K., Cheung, K.-K., Phillips, D. L., & Leung, K.-H. (2000). *Angew. Chem., Int. Ed.*, *39*, 4084.
[13] Vogler, A. & Kunkely, H. (2002). *Coord. Chem. Rev.*, *230*, 243.
[14] Aconta, A., Zink, J. I., & Cheon, J. (2000). *Inorg. Chem.*, *39*, 427.
[15] Ranjan, S. & Dikshit, S. K. (1998). *Polyhedron*, *17*, 3071.
[16] Zhaung, Q., Zhou, Q., Cheng, Y., Wang, L., Ma, D., Jing, X., & Wang, F. (2004). *Adv. Mater.*, *16*, 432.
[17] Kuang, S. M., Cuttell, D. G., McMillin, D. R., Fanwick, P. E., & Walton, R. A. (2002). *Inorg. Chem.*, *41*, 3313.
[18] Fouad, B., Michel, L., & Didier, B. (2000). *Tetrahedorn Lett*, *41*, 1539.
[19] Katritzky, A. & Laurenzo, K. (1988). *J. Org. Chem.*, *53*, 3978.
[20] Song, D., Jia, W. L., Wu, G., & Wang, S., (2005). *Dalton Trans.*, *433*.
[21] Zacharias, P. S. & Masood, M. A. (1991). *J. Chem. Soc., Dalton. Trans.*, 111.
[22] Vogler, C., Kaim, W., & Hausen, H.-D. Z. (1993). *Naturforsch.*, *48b*, 1470.