Polyhedron 30 (2011) 1871-1875

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis, characterization and luminescence properties of copper(I) complexes containing 2-phenyl-3-(benzylamino)-1,2-dihydroquinazolin-4(3H)-one and triphenylphosphine as ligands

S.S. Chavan^{a,*}, G.A. Gaikwad^a, V.A. Sawant^a, G.K. Lahiri^b

^a Department of Chemistry, Shivaji University, Kolhapur, MS 416004, India ^b Department of Chemistry, Indian Institute of Technology, Bombay 400076, India

ARTICLE INFO

Article history: Received 9 March 2011 Accepted 17 April 2011 Available online 3 May 2011

Keywords: Copper(I) complexes Crystal structure Electrochemistry Luminescence properties

ABSTRACT

Some copper(I) complexes of the formula $[Cu(L)(PPh_3)_2]X$ (**1–4**) [where **L** = 2-phenyl-3-(benzylamino)-1,2-dihydroquinazolin-4(3H)-one; PPh₃ = triphenylphosphine; X = Cl⁻, NO₃⁻, ClO₄⁻ and BF₄⁻] have been prepared and characterized on the basis of elemental analysis, IR, UV–Vis and ¹H NMR spectral studies. The representative complex of the series **4** has been characterized by single crystal X-ray diffraction which reveal that in the complex the central copper(I) ion assumes the irregular distorted-tetrahedral geometry. Cyclic voltammetry of the complexes indicate a quasireversible redox behavior corresponding to Cu(II)/Cu(I) couple. All the complexes exhibit intraligand ($\pi \rightarrow \pi^*$) fluorescence with high quantum yield in dichloromethane solution.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The coordination chemistry of monovalent copper(I) complexes is currently receiving much interest mainly due to their potential applications in organic light-emitting diodes (OLEDs) [1,2], supramolecular assemblies [3], chemical sensors [4], display devices [5], photovoltaic cells [6], biological probing and oxygen sensing [7], etc. Due to the favorable soft acid-soft base interaction, the coordination chemistry of this closed-shell d¹⁰ metal ion is largely based upon the coordination of the ligands such as various N, S, P and halide donor ligands. The steric, electronic and conformational effects imparted by the coordinated ligands play an essential role in stabilizing the copper(I) state and modifying the physical and chemical properties of the prepared complexes. Copper(I) complexes with N, S, P potentially donor ligands have been extensively studied due to their wide variation in structural motifs and rich photophysical properties [8-10], however, only few complexes with O-donor ligands are synthesized and structurally characterized [11,12]. Among the various ligands quinazolinone havereceived much more attention due to its diverse range of pharmacological properties [13,14] and applications in several areas such as electronics, anticorrosive agents, polymers, optical materials and fluorescent tags in DNA sequencing [15-17]. Recently guinazolin-4(3H)-ones have been found to possess potent central nervous system activities including analgesic, antiinflammatory and anti-convulsant effects [18,19]. In addition, condensed quinazolinones have drawn special attention due to their flexibility, preparative accessibility, diversity, structural variability and selectivity and sensitivity towards the coordinated metal [20,21]. Because of the wide utility of quinazolinone derivatives in biological and pharmaceutical activities and their ability to act as polyfunctional ligands, many studies on their metal complexes have been carried out [22–24].

In this paper, we report the synthesis of some copper(I) complexes **1–4** derived from 2-phenyl-3-(benzylamino)-1,2-dihydroquinazolin-4(3H)-one and triphenylphosphine as ligands. All the complexes are characterized by elemental analysis, spectroscopy and compound **4** also by X-ray crystallography. The photoluminescence properties and electrochemical behavior of the complexes are also discussed.

2. Experimental

2.1. General methods

All chemicals used were of reagent grade and used as received. 2-Phenyl-3-(benzylamino)-1,2-dihydroquinazolin-4(3H)-one (L) was prepared as previously reported [25]. The copper(I) compounds CuCl [26], Cu(PPh₃)₂NO₃ [27], [Cu(MeCN)₄]ClO₄ [28] and [Cu(MeCN)₄]BF₄ [29] were prepared according to the literature procedure.

Microanalysis (C, H and N) were performed on a Thermo Finnegan FLASH EA-112 CHNS analyzer. Infrared spectra were recorded





^{*} Corresponding author. Tel.: +91 231 2609164; fax: +91 231 2691533. *E-mail address:* sanjaycha2@rediffmail.com (S.S. Chavan).

^{0277-5387/\$ -} see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2011.04.038

on Perkins Elmer FTIR spectrometer as KBr pellets in the 4000– 400 cm^{-1} range. Electronic spectra were recorded in dichloromethane (10^{-4} M) on Shimadzu UV–Vis–NIR spectrophotometer. ¹H NMR spectra of the samples dissolved in CDCl₃ were measured on AMX-400 MHz instrument using TMS [(CH₃)₄Si] as an internal standard of chemical shifts (ppm). Luminescence properties were measured using a JASCO F.P.750 fluorescence spectrophotometer equipped with quartz cuvette of 1 cm³ path length at room temperature. Cyclic voltammetry measurements were performed with Electrochemical Quartz Crystal Microbalance CHI-400. A standard three electrode system consisting of Pt disk working electrode, Pt wire counter electrode and Ag/AgCl reference electrode containing aqueous 3 M KCl were used. All potentials were converted to SCE scale.

2.2. Synthesis of copper(I) complexes (1-4)

2.2.1. [Cu(L)(PPh₃)₂]Cl (1)

To a 10 ml acetonitrile solution of CuCl (1 mmol, 0.0989 g), 2 equivalent triphenylphosphine (2 mmol, 0.522 g) were added and solution was stirred for 30 min. The solvent was evaporated under vacuum at room temperature. The crystalline product of $[Cu(MeCN)_2(PPh_3)_2]$ Cl obtained was added to a stirring solution of ligand **L** (1 mmol, 0.327 g) in 10 ml dichloromethane and stirred for 2 h at room temperature. The volume of the solvent was reduced under vacuum. The light yellow-green colored complexes were developed by diffusion of diethyl ether into the filtrate.

2.2.1.1. Complex **1**. Yield 88%; m.p. 182 °C; elemental analysis (C, H and N, wt.%). *Anal.* Calc. for $C_{57}H_{45}N_3OP_2CICu:$ C, 71.99; H, 4.98; N, 4.42. Found: C, 71.64; H, 4.76; N, 4.58%. IR (KBr) (cm⁻¹): 1623, v(C=O); 1586, v(HC=N); 1479, 1434, 693, 519, v(PPh_3); UV-Vis (CH₂Cl₂) λ_{max} (nm): 266, 286, 342; ¹H NMR (CDCl₃) (400 MHz): δ 9.18 (s, HC=N), δ 6.67–8.60 (m, Ar-H).

2.2.2. $[Cu(L)(PPh_3)_2]NO_3$ (2)

To a solution of $[Cu(PPh_3)_2]NO_3$ (1 mmol, 0.327 g) in CH_2Cl_2 (10 ml) was added a solution of ligand L (1 mmol, 0.327 g) in CH_2Cl_2 (10 ml) and stirred for 2 h at room temperature. The volume of the solvent was reduced under vacuum at room temperature. The light yellow colored complexes were developed by the diffusion of diethyl ether in to the filtrate.

2.2.2.1. Complex **2**. Yield 86%; m.p. 178 °C; elemental analysis (C, H and N, wt.%). *Anal.* Calc. for $C_{57}H_{45}N_4O_4P_2Cu$: C, 70.04; H, 4.85; N, 5.73. Found: C, 69.92; H, 4.64; N, 5.88%. IR (KBr) (cm⁻¹): 1623, v(C=O); 1586, v(HC=N); 1479, 1434, 693, 519, v(PPh_3); UV-Vis (CH₂Cl₂) λ_{max} (nm): 276, 284, 348; ¹H NMR (CDCl₃) (400 MHz): δ 9.20 (s, HC=N), δ 6.99–8.20 (m, Ar-H).

2.2.3. [Cu(L)(PPh₃)₂]ClO₄ (3)

The complex **3** was prepared similar to the procedure performed in the preparation of **1** except that CuCl was replaced by $[Cu(MeCN)_4]ClO_4$ (1 mmol, 0.327 g).

2.2.3.1. Complex **3**. Yield 92%, m.p. 186 °C; elemental analysis (C, H and N, wt.%). Anal. Calc. for $C_{57}H_{45}N_3O_5P_2CICu: C, 67.45; H, 4.67; N, 4.14. Found: C, 67.25; H, 4.55; N, 4.72%. IR (KBr) (cm⁻¹): 1622, v(C=O); 1583, v(HC=N) 1480, 1434, 695, 517, v(PPh_3); 1094, 623 v(CIO₄); UV–Vis (CH₂Cl₂) <math>\lambda_{max}$ (nm): 274, 294, 358; ¹H NMR (CDCl₃) (400 MHz): δ 9.17 (s, HC=N), δ 6.30–7.89 (m, Ar-H).

2.2.4. [Cu(L)(PPh₃)₂]BF₄ (4)

The complex **4** was prepared similar to the procedure performed in the preparation of **1** except that CuCl was replaced by $[Cu(MeCN)_4]BF_4$ (1 mmol, 0.314 g). 2.2.4.1. Complex **4**. Yield 88%, m.p. 172 °C; elemental analysis (C, H and N, wt.%). *Anal.* Calc. for $C_{57}H_{45}N_3OP_2F_4BCu$: C, 68.30; H, 4.73; N, 4.19. Found: C, 67.98; H, 4.56; N, 4.38%. IR (KBr) (cm⁻¹): 1611, v(C=O); 1581, v(HC=N) 1481, 1435, 690, 517, v(PPh_3); 1094, v(BF_4); UV-Vis (CH_2Cl_2) λ_{max} (nm): 256, 290, 350; ¹H NMR (CDCl_3) (400 MHz): δ 9.20 (s, HC=N), δ 6.99–8.60 (m, Ar-H).

2.3. X-ray diffraction study

The single crystals of complex **4** suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into solution of complex in dichloromethane. The intensity data were collected on a Nonius MACH-3 four-circle diffractometer with graphite-monochromatized Mo K α radiation. The details of crystal data, data collection and, the refinement are given in Table 1. The structure was solved by direct method using the SHELXS 93 program and refined by using SHELXL 97 software [30]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms were geometrically fixed and refined using a riding model.

3. Results and discussion

The reaction of two equivalent of trlphenylphosphine with copper(I) salt followed by the addition of one equivalent of quinazolinone ligand **L** in dichloromethane solution at room temperature afforded monomeric complexes of the type $[Cu(L)(PPh_3)_2]X$ [where **L** = 2-phenyl-3-(benzylamino)-1,2-dihydroquinazolin-4(3H)-one; PPh₃ = triphenylphosphine; X = Cl⁻, NO₃⁻, ClO₄⁻ and BF₄⁻]. All the complexes are microcrystalline solids that are soluble in common organic solvents like dichloromethane, chloroform, acetonitrile, methanol, ethanol, etc. The results of elemental analysis (C, H and N) which are given in Section 2 confirm the assigned composition of the complexes.

Table 1	l		
Crystal	data and structure refinem	ents details for co	omplex [Cu(L)(PPha)a]

Frystal data and structure refinements details for complex $[Cu(L)(PPh_3)_2]BF_4$ (4).			
Empirical formula	C ₅₇ H ₄₅ BCuF ₄ N ₃ OP ₂		
Formula weight	1000.25		
Т (К)	150(2)		
Wavelength (Å)	0.71073		
Crystal system	triclinic		
Space group	PĪ		
a (Å)	12.8591(5)		
b (Å)	13.7884(10)		
c (Å)	15.8076(7)		
α (°)	106.882(5)		
β(°)	97.097(4)		
γ (°)	109.548(5)		
V (Å ³)	2450.5(2)		
Ζ	2		
$D_{\text{calc}} (\text{mg/m}^3)$	1.356		
F(0 0 0)	1032		
Absorption coefficient (mm ⁻¹)	0.570		
θ Range for data collection (°)	3.35-25.00		
Completeness to θ = 25.00	99.8%		
Crystal size (mm)	$0.33 \times 0.28 \times 0.21$		
Reflections collected/unique	17 744/8615		
R _{int}	0.0464		
Limiting indices	$-15\leqslant h\leqslant 15,-14\leqslant k\leqslant 16,$		
	$-18 \leqslant l \leqslant 18$		
Absorption correction	semi-empirical from equivalents		
Maximum and minimum transmission	0.8896 and 0.8341		
Data/restraints/parameters	8615/0/622		
Refinement method	full-matrix least-squares on F^2		
Goodness-of-fit on F ²	0.931		
Final R indices $[I > 2\sigma(I)] R_1$, wR_2	0.0563, 0.1366		
R indices (all data) R_1 , wR_2	0.0993, 0.1465		
Largest difference in peak and hole $(e A^{-3})$	1.397 and –0.657		

3.1. Spectroscopic properties

The IR frequencies of selected groups in the spectra of complexes are given in Section 2. The medium intensity band at 3283 cm⁻¹ observed in the IR spectrum of free ligand **L** is due to the v(NH) of the quinazoline ring. This band shifted to higher energies, by 11–15 cm⁻¹ in all of the complexes indicates noninvolvement of the N–H in coordination. The characteristic v(C=0)frequency of ligand L occurs at 1660 cm⁻¹ shifted to lower frequency at 1611–1623 cm⁻¹ in all complexes providing strong evidence for involvement of carbonyl oxygen in complexation with metal ion [22]. The band at 1618 cm^{-1} in the spectrum of free ligand **L** attributed to the azomethine v(C=N) group. In the spectra of the complexes this band shifted to lower frequency as a result of coordination through the azomethine nitrogen atom [31]. This was also confirmed by the appearance of new band at \sim 530 cm⁻¹ in complexes due to v(Cu-N). The spectra of all the copper(I) complexes exhibit the expected bands due to PPh₃ ligand at around 1434, 742, 692, 506 cm $^{-1}$. The strong band observed at 1374 cm⁻¹ as well as medium intensity band at 820 cm⁻¹ in the spectra of the complex **2** assigned for presence of ionic nitrate in the complex [32]. The perchlorate complex **3** shows a broad band at 1093 cm⁻¹ (v_3) and a strong band at 622 cm⁻¹ (v_4) is devoid of any splitting suggesting that the ClO₄⁻ anion is not coordinated to the copper atom [33]. However, a broad band observed at 1094 cm⁻¹ in complex **4** corresponds to presence of BF_4^- anion in the complex [34].

The electronic spectra of all copper(I) complexes (**1–4**) in dichloromethane (10^{-4} M) were measured at room temperature. In the spectra of complexes no d–d transitions are expected, the UV–Vis band observed at 342–358 nm is assigned to ligand-originating intra-ligand transition together with some metal-ligand charge transfer (MLCT) character [35]. The high energy bands located in the UV region of the complexes at 256–274 and 284–294 nm are assigned to intraligand π – π * transitions.

The ¹H NMR spectral data of all copper(I) complexes (**1–4**) in CDCl₃ are given in Section 2. In complexes **1–4** the resonances of phenyl protons of the coordinated PPh₃ ligands overlap to some extent with those of the phenyl hydrogen atoms of ligand **L**. However, the broad multiplet observed in the range δ 6.30–8.60 ppm for all the complexes were assigned to the phenyl group of PPh₃ together with ring protons of ligand **L**. Aside from the aromatic protons, the imine proton appears as a singlet at about δ 9.20 ppm in the spectra of all complexes. The downfield shift of the imine proton in the complexes relative to the free ligand **L** can be attributed to the deshielding effect resulting from the coordination of the ligand [36].

3.2. Crystal structure

The crystals of $[Cu(L)(PPh_3)_2]BF_4$ (**4**) were grown by slow diffusion of diethyl ether into a solution of complex in dichloromethane and structure was determined by X-ray crystallography. X-ray analysis revealed that the complex **4** crystallizes in the triclinic space group $P\bar{1}$. The crystal of complex **4** contains discrete cation $[Cu(L)(PPh_3)_2]^*$ and tetrafluoroborate counter anion. The molecular structure of **4** along with the atom numbering scheme is illustrated in Fig. 1 and selected bond lengths and bond angles are collected in Table 2.

The complex is mononuclear and central copper(I) ion exhibit highly distorted tetrahedral geometry with $CuNOP_2$ coordination. The quinazoline ligand is chelated to the copper ion in neutral bidentate form through azomethine nitrogen and carbonyl oxygen forming a five-membered chelation ring. The distorted four-coordinate geometry of copper(I) is completed by two triphenylphosphine ligands. The largest deviation from the ideal tetrahedral geometry is reflected by the restricted bite angles of the chelating



Fig. 1. Molecular structure of [Cu(L)(PPh₃)₂]BF₄ (4).

Table 2	
Selected bond lengths (Å) and bo	nd angles (°) for complex A

Cu(1)—O(1)	2.123(3)
Cu(1)-N(1)	2.123(4)
Cu(1)—P(2)	2.2460(12)
Cu(1)-P(1)	2.2476(11)
N(2)-C(1)	1.360(6)
N(2)-C(8)	1.511(7)
N(3)-C(7)	1.370(7)
N(3)-C(8)	1.482(7)
O(1)-Cu(1)-N(1)	76.53(12)
O(1)-Cu(1)-P(2)	101.86(8)
N(1)-Cu(1)-P(2)	114.77(10)
O(1)-Cu(1)-P(1)	108.41(8)
N(1)-Cu(1)-P(1)	112.93(10)
P(2)-Cu(1)-P(1)	127.91(5)
C(15)-N(1)-N(2)	116.7(4)
C(15)-N(1)-Cu(1)	132.1(3)
N(2)-N(1)-Cu(1)	110.5(3)
N(3)-C(8)-C(9)	111.3(5)
N(3)-C(8)-N(2)	106.2(5)
C(9)-C(8)-N(2)	110.7(5)
C(15)-N(1)-N(2)	116.7(4)
C(15)-N(1)-Cu(1)	132.1(3)
N(2)-N(1)-Cu(1)	110.5(3)
C(1)-N(2)-N(1)	116.9(4)
C(1)-N(2)-C(8)	126.1(4)
N(1) - N(2) - C(8)	116.7(4)

ligands. The intraligand O(1)-Cu(1)-N(1) chelate angle, 76.53(12)° is much less than 109.4°. However, the P(2)-Cu(1)-P(1), 127.91(5)° angle have opened up due to the steric effects from the bulky PPh₃ ligands. The average Cu-N and Cu-P bond distances are 2.123 and 2.246 Å, respectively, and are

comparable to those reported for $[Cu(A)(PPh_3)_2]CIO_4$ (2.098 and 2.251 Å) [37].

Torsion angles in the chelating ring and quinazoline group are listed in Table 3. The chelating ring Cu(1)-N(1)-N(2)-C(1)-O(1) is nearly planar with sum of three N atom bond angles is 359.3°. However, some strain in the chelate ring is suggested by the deviation from the 120° angle about the N atom Cu(1)-N(1)-C(15), 132.1(3)°; Cu(1)-N(1)-N(2), 110.5(3)° and C(15)-N(1)-N(2), 116.7(4)°.

In the heteroatomic part of quinazoline, the angles N(3)-C(8)-C(9), 111.3(5); N(3)-C(8)-N(2), 106.2(5) and C(9)-C(8)-N(2), 110.7(5); indicate the sp³ hybridized state of the carbon atom, and the geometry around C(8) can be viewed in terms of a distorted tetrahedral geometry. The two N–C (sp²) bond distances [N(2)-C(1), 1.360(6) and N(3)-C(7), 1.370(7)] show double bond character and two N-C (sp³) bond distances [N(2)–C(8), 1.511(7) and N(3)–C(8), 1.482(7)] show single bond character. The sum of the angles around N(2) and N(3) are 359.7° and 360.0°, respectively. The benzaldehyde moiety directly linked at C(8) is oriented at an angle of $83.7(7)^\circ$ with respect to the quinazoline ring. The quinazoline ring and the benzaldehyde moiety linked through N(1) and C(15) are trans to each other, thus show-E-configuration. Further, the tortional angle of ing N(2)-N(1)-C(15)-C(16) is 175.2(3)° indicating an anti-periplanar arrangement.

3.3. Electrochemistry

The electrochemical properties of the copper(I) complexes have been examined cyclic voltammetrically in 10^{-3} M CH₂Cl₂ solution containing 0.05 M *n*-Bu₄NClO₄ as supporting electrolyte and redox potentials are expressed with reference to Ag/AgCl. All the measurements were carried out in the potential range +1.5––1.5 V with scan rate 50 mV s⁻¹. The results were collected in Table 4.

The electrochemical potentials of the copper(I) complexes were characterized by well-defined redox process in positive potential side. Since the ligand used in this work is not reversibly oxidized or reduced in the applied potential range, the redox processes are assigned to the metal centers only. For all the copper(I) complexes the reduction wave (E_{pc} , 0.673–0.720 V) corresponding to reduction of Cu(II) to Cu(I) is obtained. During the reverse scan the oxidation of Cu(I) to Cu(II) occurs in the potential range (E_{pa} , 0.542–0.576 V). The quasireversible character is accounted from the values of the limiting peak-to-peak separation (ΔE_p) ranging from 118 to 162 mV under the conditions of measurements.

3.4. Fluorescence spectral studies

The photoluminescence properties of the ligand **L** and its copper(I) complexes (**1–4**) were studied at room temperature in dichloromethane solution. The emission spectra of copper(I) complexes are depicted in Fig. 2 and data are collected in Table 5. The ligand **L** exhibit very weak fluorescence signal centered at 413 nm with an excitation maxima at 303 nm. The emission observed in the ligand **L** can be assigned to $\pi \rightarrow \pi^*$ electron transition.

 Table 3

 Torsion angles for chelating ring and quinazolinone group.

Cu(1)-N(1)-N(2)-C(1)	-4.8(4)
Cu(1) - O(1) - C(1) - N(2)	8.8(5)
N(1)-N(2)-C(1)-O(1)	-2.6(6)
O(1)-Cu(1)-N(1)-N(2)	6.6(2)
N(1)-Cu(1)-O(1)-C(1)	-8.4(3)
N(3)-C(8)-C(9)-C(10)	83.7(7)
N(2)-N(1)-C(15)-C(16)	175.2(3)

Table 4

Electrochemical data for copper(I) complexes.

Compound	$E_{\rm pa}\left({\rm V}\right)$	$E_{\rm pc}\left({\sf V}\right)$	$\Delta E_{\rm p}~({\rm mV})$	$E_{1/2}$ (V)
1 2 3	0.706 0.673 0.694	0.557 0.542 0.576	149 131 118	0.631 0.608 0.635
4	0.720	0.558	162	0.639

Supporting electrolyte: *n*-Bu₄NCIO₄ (0.05 M); complex: 0.001 M; solvent: DMF; $\Delta E_p = E_{pa} - E_{pc}$ where, E_{pa} and E_{pc} are anodic and cathodic potentials, respectively; $E_{1/2} = \frac{1}{2} (E_{pa} + E_{pc})$; scan rate: 50 mV s⁻¹.



Fig. 2. Normalized emission spectra of the copper(I) complexes (1-4).

Table 5Fluorescence spectral data of L and its copper(I) complexes.

0.004
0.004
0.086
0.082
0.084
0.091

However, all the copper(I) complexes gives strong fluorescence with high quantum yield in dichloromethane solution. The copper(I) complexes **1–4** show blue to bluish-green emission band with a maximum wavelength at 420–504 nm upon excitation at 386–392 nm. The fluorescence emission observed in the complexes is assigned to intra-ligand ($\pi \rightarrow \pi^*$) transition [38]. The red shift in fluorescence emission of the complexes in comparison to that of the free ligand **L** can be attributed to the coordination of ligand to the copper(I) ions which effectively increases the rigidity of the ligands and reduces the loss of energy via radiation less thermal vibrational decay [39]. Further, the presences of counter anions show a pronounced effect on the emission energy of the complexes (Fig. 2). The emission energy decreases in the following sequence: **2** (NO₃⁻) > **1** (Cl⁻) > **3** (ClO₄⁻) > **4** (BF₄⁻).

The fluorescence quantum yield (Φ) of the complexes was determined by using the quinine sulfate as a reference with known $\Phi_{\rm R}$ of 0.52 and appeared at 0.080–0.091. The area of emission spectrum was integrated using the software available in the instrument and quantum yield was calculated according to the following equation.

$$\Phi_{\rm S} = A_{\rm S}/A_{\rm R} \times ({\rm Abs})_{\rm R}/({\rm Abs})_{\rm S} \times \Phi_{\rm R} \tag{1}$$

Here Φ_S and Φ_R are the fluorescence quantum yield of the sample and reference, respectively. A_S and A_R are the area under the fluorescence spectra of the sample and reference, respectively. (Abs)_S and (Abs)_R are the respective optical densities of the sample and the reference solution at the wavelength of excitation.

4. Conclusions

Some copper(I) complexes **1–4** containing 2-phenyl-3-(benzylamino)-1,2-dihydro quinazolin-4(3H)-one and triphenylphosphine have been prepared. The structure of all copper(I) complexes were confirmed on the basis of elemental analysis, FTIR, UV–Vis and ¹H NMR spectroscopy. The single crystal X-ray diffraction study of complex **4** reveals that the central copper(I) ion assumes highly distorted tetrahedral geometry. Cyclic voltammetry studies of the complexes indicate quasireversible redox behavior corresponding to Cu(II)/Cu(I) couple. All the complexes exhibit blue to blue-green emission in dichloromethane solution at room temperature assigned to intra-ligand ($\pi \rightarrow \pi^*$) transitions.

Acknowledgements

We acknowledge Indian Institute of Science (IISc), Bangalore for providing elemental analysis and ¹H NMR facilities.

Appendix A. Supplementary data

CCDC 784048 contains the supplementary crystallographic data for $[Cu(L)(PPh_3)_2]BF_4$ (**4**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] W.L. Jia, T. McCormick, Y. Tao, J.P. Lu, S. Wang, Inorg. Chem. 44 (2005) 5706.
- [2] Q.S. Zhang, Q.G. Zhou, Y.X. Cheng, L.X. Wang, D.G. Ma, X.B. Jing, F.S. Wang, Adv. Mater. 16 (2004) 432.
- [3] W. Wei, M. Wu, Q. Gao, Q. Zhang, Y. Huang, F. Jiang, M. Hong, Inorg. Chem. 48 (2009) 420.

- [4] S.B. Harkins, J.C. Peters, J. Am. Chem. Soc. 127 (2005) 2030.
- [5] G. Che, Z. Su, W. Li, B. Chu, M. Li, Appl. Phys. Lett. 89 (2006) 103511.
- [6] T. Bessho, E.C. Constable, M. Graetzel, A.H. Redondo, C.E. Housecroft, W. Kylberg, M.K. Nazeeruddin, M. Neuburger, S. Schaffner, Chem. Commun. (2008) 3717.
- [7] L. Shi, B. Li, S. Yue, D. Fan, Sens. Actuators B, Chem. 137 (2009) 386.
- [8] X. Li, J. Ding, W. Jin, Y. Cheng, Inorg. Chim. Acta 362 (2009) 233.
- [9] M. Mamais, P.J. Cox, P. Aslanidis, Polyhedron 27 (2008) 175.
- [10] T. McCormic, W.-L. Jia, S. Wang, Inorg. Chem. 45 (2006) 147.
- [11] D.T. Darensbourg, D.L. Larkins, J.H. Reibenspies, Inorg. Chem. 37 (1998) 6125.
 [12] D. Li, R.-Z. Li, Z. Ni, Z.-Y. Qi, X.-L. Feng, J.-W. Cai, Inorg. Chem. Commun. 6
- (2003) 469. [13] Martin J. Deetz, Jeremiah P. Malerich, Alicia M. Beatty, Bradley D. Smith,
- Tetrahedron Lett. 42 (2001) 1851.
- [14] Y. Zhang, Z. Chen, Y. Lou, Y. Yu, Eur. J. Med. Chem. 44 (2009) 448452.
- [15] K.P. Chan, H. Yang, A.S. Hay, J. Polym. Sci. 34 (1996) 1923.
- [16] V.G. Chapoulaud, N. Ple, A. Turck, G. Queguiner, Tetrahedron 56 (2000) 5499.
 [17] T. Herget, M. Freitag, M. Morbitzer, R. Kupfer, T. Stamminger, M. Marschall, Antimicrob. Agents Chemother. 48 (2004) 4154.
- [18] R.V. Chambhare, B.G. Khadse, A.S. Bobde, R.H. Behekar, Eur. J. Med. Chem. 38 (2003) 89.
- [19] V. Algarsamy, S. Murugesan, R.V. Sheorey, Med. Chem. Res. 17 (2008) 564.
- [20] S. Chandra, S. Raizada, M. Tyagi, A. Gautam, Bioinorg. Chem. Appl. 1 (2007) ID-51483.
- [21] B. Samanta, J. Chakraborty, C.R. Choudhury, S.K. Dey, D.K. Dey, S.R. Batten, P. Jensen, G.P.A. Yap, S. Mitra, Struct. Chem. 18 (2007) 33.
- [22] I.M. El-Mehasseb, A. El-Motaleb, M. Ramadan, Transition Met. Chem. 31 (2006) 730.
- [23] K.B. Gudasi, S.A. Patil, R.S. Vadavi, R.V. Shenoy, Transition Met. Chem. 31 (2006) 586.
- [24] K.B. Gudasi, S.A. Patil, M.V. Kulkarni, M. Nethaji, Transition Met. Chem. 34 (2009) 325.
- [25] V.A. Sawant, B.A. Yamgar, S.K. Sawant, S.S. Chavan, Spectrochem. Acta 74A (2009) 1100.
- [26] P.H. Davis, R.L. Belford, I.C. Paul, Inorg. Chem. 12 (1973) 213.
- [27] F.A. Cotton, D.M.L. Goodgame, J. Chem. Soc. (1960) 5267.
- [28] D. Datta, A. Chakravorty, Inorg. Chem. 22 (1983) 1085.
- [29] G.J. Kubas, B. Monzyk, A.L. Crumbliss, Inorg. Synth. 19 (1978) 1437.
- [30] G.M. Sheldric, Siemens SHELXTL, Version 5.03; Siemens Crystallographic Research Systems, Madison, WI 53719, 1994.
- [31] S.J. Scales, H. Zhang, P.A. Chapman, C.P. McRory, E.J. Derrah, C.M. Vogels, M.T. Saleh, A. Decken, S.A. Westcott, Polyhedron 23 (2004) 2169.
- [32] P. Karagiannidis, P. Aslandis, S. Papastefanou, D. Mentzafos, A. Hountas, A. Terzis, Inorg, Chim. Acta 156 (1989) 265.
- [33] Z. Travnicek, R. Pastorek, V. Slovak, Polyhedron 27 (2008) 411.
- [34] K. Nakamoto, Infrared and Raman Spectra on Inorganic and Coordination
- Complexes, fourth ed., John Wiley and Sons, USA, 1992.
- [35] A. Kaltzoglou, P.J. Cox, P. Aslanidis, Inorg. Chim. Acta 358 (2005) 3048.
- [36] M. Amirnasar, G. Kickelbick, S. Dehghanpour, Helv. Chim. Acta 89 (2006) 274.
- [37] S. Dehghanpour, N. Bouslimani, R. Welter, F. Mojahed, Polyhedron 26 (2007)
- 154.
- [38] N.J. Turro, Pure Appl. Chem. 49 (1977) 405.
- [39] T. Yu, K. Zhang, Y. Zhao, C. Yang, H. Zhang, L. Qian, D. Fan, W. Dong, L. Chen, Y. Qiu, Inorg. Chem. Acta 361 (2008) 233.