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Copper(I) Complexes of N-(2-{[(2E)-2-(4-Nitrobenzylidenyl) Hydrazinyl]Carbonyl}Phenyl)Benzamide and Triphenylphosphine: Synthesis, Characterization and Luminescence Properties

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Abstract Copper(I) complexes of the formula $[Cu(L)(PPh_3)_2]$ X (1-4) (X = Cl(1), ClO₄(2), BF₄(3) and PF₆(4)) [where $L = N-(2-\{[(2E)-2-(4-nitrobenzylidenyl)hydrazinyl]\}$ carbonyl}phenyl)benzamide; $PPh_3 = triphenylphosphine$] have been prepared by the condensation of N-[2-(hydrazinocarbonyl)phenyl]benzamide with 4nitrobenzaldehyde followed by the reaction with CuCl, [Cu(MeCN)₄]ClO₄, [Cu(MeCN)₄]BF₄ and [Cu(MeCN)₄]PF₆ in presence of triphenylphosphine as a coligand. Complexes 1-4 were then characterized by elemental analyses, FTIR, UV-visible and ¹H NMR spectroscopy. Mononuclear copper(I) complexes 1-4 were formed with L in its keto form by involvement of azomethine nitrogen and the carbonyl oxygen along with two PPh3 groups. A single crystal X-ray diffraction study of the representative complex $[(Cu(L)(PPh_3)_2]CIO_4$ (2) reveals a distorted tetrahedral geometry around Cu(I). Crystal data of (2): space group = C2/c, a = 42.8596 (9) Å, b = 14.6207 (3) Å, c = 36.4643 (7) Å, V = 20,653.7 (7) Å³, Z = 16. Complexes 1–4 exhibit quasireversible redox behaviour corresponding to a Cu(I)/Cu(II) couple. All complexes show blue-green emission as a result of fluorescence from an intra-ligand charge transition (ILCT), ligand to ligand charge transfer transition (LLCT) or mixture of both. Significant

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² Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia increase in size of the counter anion shows marked effect on quantum efficiency and lifetime of the complexes in solution.

Keywords Copper(I) complexes · Crystal structure · Luminescence properties

Introduction

Copper(I) complexes have attracted considerable attention on account of their unusual structural features, utility in solar energy and supramolecular devices, luminescent properties, catalytic and biological relevance [1-4]. They are environmentally friendly, less expensive and possesses intriguing coordination modes and exhibit a wide range of photochemical and photophysical properties [5, 6]. Owing to favourable soft acid-soft base interaction, the chemistry of this closed-shell d¹⁰ metal ion is largely depends upon the mode of coordination of the ligands. The steric, electronic and conformational effects imparted by these 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 [7–9]. However, only a few complexes with O-donor ligands have been synthesized and structurally characterized [10, 11]. Among the various ligands hydrazone represent as an important series of Schiff bases which contain several potential donor sites and so act as major polydentate ligands. They play an important role in medicinal chemistry and have a wide range of applications in catalysis, medicine, corrosion and analytical chemistry as well as in functional materials [12–14]. As they have a wide range of biological and pharmaceutical activities and a strong tendency to chelate with transition metals [15], lanthanide metals [16] and main group metals [17], the coordination chemistry of hydrazone has been intensively investigated. Acylhydrazone particularly, which contains the ketotype structure (-O = C-N-N = C-) are useful ligands for the construction of novel coordination compounds with diverse structures due to the multiple active coordination sites and rich coordination modes. Also, they are capable of yielding supramolecular architecture and polymeric materials featuring bridging and oxobridging. Metal complexes of acylhydrazone have proven to have potential applications as catalysts [18], luminescent probes [19] and molecular sensors [20]. More recently hydrazone chelators have been used in the treatment of iron overload diseases such as β -thalasemia [21].

In this paper, we report the synthesis of some copper(I) complexes (1–4) derived by the reaction of N-(2-{[(2E)-2-(4-nitrobenzylidenyl)hydrazinyl]carbonyl}phenyl) benzamide with CuCl, $[Cu(CH_3CN)_4]ClO_4$, $[Cu(CH_3CN)_4]BF_4$ and $[Cu(CH_3CN)_4]PF_6$ in the presence of triphenylphosphine. All the compounds were characterized by elemental analysis, spectroscopic techniques and compound **2** by X-ray crystallography. The electrochemical and luminescent properties of the complexes are also reported.

Experimental

General Methods

All chemicals used were of reagent grade and used as received. N-(2-Hydrazinocarbonyl-phenyl)-benzamide was prepared as previously reported [22]. The copper(I) compounds CuCl [23], [Cu(MeCN)_4]ClO_4 [24], [Cu(MeCN)_4]BF_4 [25] and Cu(MeCN)_4PF_6 [26] were prepared according to literature procedures.

Elemental analyses (C, H and N) of the copper(I) complexes were conducted on Thermo Finnegan FLASH EA-1112 CHNS analyzer. IR spectra were recorded on a Perkin-Elmer-100 FTIR Spectrometer. ¹H NMR spectra of the samples dissolved in CDCl3 were measured on a Bruker 300 MHz instrument using TMS [(CH₃)₄Si] as an internal standard of chemical shifts (ppm). Electronic spectra were recorded in dichloromethane (10⁻⁴ M) on a Shimadzu 3600 UV-Vis-NIR spectrophotometer. Emission spectra were recorded using a Perkin-Elmer LS 55 spectrofluorometer equipped with quartz cuvettes of 1 cm³ path length at room temperature. Mass spectra were measured on a GCMS Shimadzu-2010. Luminescence lifetime measurements were carried out by using time-correlated single photon counting on HORIBA Jobin Yvon. Thermal analysis of the complexes was carried out in nitrogen atmosphere at a heating rate of 10 °C/min on a Perkin-Elmer thermal analyzer. Cyclic voltammetry measurements were performed with a CH-400 A electrochemical analyzer. Tetrabutyl ammonium perchlorate (TBAP) was used as the supporting electrolyte and all measurements were carried out in CH_2Cl_2 solution at room temperature with a scan rate of 100 mVs^{-1} .

Synthesis of Ligand (L)

N-(2-{[(2E)-2-(4-nitrobenzylidenyl)hydrazinyl]carbonyl} phenyl)benzamide (L) was prepared by adopting and modifying the method described in the literature [27]. An intimate mixture of N-[2-(hydrazinocarbonyl)phenyl]benzamide (1 mmol, 0.255 g) and 4-nitrobenzaldehyde (1 mmol, 0.151 g) in ethanol (20 ml) was refluxed for 5 h in the presence of a few drops of acetic acid. On partial removal of the solvent the product obtained was filtered, washed with ethanol and dried in vacuo.

Yield: 91 %; Elemental analyses (C, H, N, wt%) Anal. Calc. for C₂₁H₁₆N₄O₄: C,64.94; H, 4.15, N, 14.43; found: C, 64.90; H, 4.05; N, 14.60; IR (KBr; cm⁻¹); 3248, ν (NH); 1686, ν (C = O); 1618, ν (HC = N); ¹H NMR (CDCl₃; 300 MHz): δ 8.26 (s, 1H, HC = N), δ 10.30 (s, N-NHCO), δ 8.56 (s, C₆H₅CONH), δ 6.65–8.18 (m, phenyl); MS(EI): m/e 388.12 (M+).

Synthesis of [Cu(L)(PPh₃)₂]Cl (1)

To a 10 ml acetonitrile solution of CuCl (1 mmol, 0.0989 g), 2 equivalent of triphenylphosphine (2 mmol, 0.522 g) were added and the solution was stirred for 30 min. The solvent was evaporated under vacuum at room temperature. The crystalline product [Cu(MeCN)₂(PPh₃)₂]Cl obtained was added to a solution of ligand L (1 mmol, 0.388 g) in 10 ml dichloromethane and stirred for 2 h at room temperature. The volume of solvent was reduced under vacuum and the solid product was produced by diffusion of diethyl ether into the filtrate.

Yield: 82 %; Elemental analyses (C, H, N, wt%) Anal. Calc. for C₅₇H₄₆CuN₄O₄P₂Cl: C,67.65; H, 4.58, N, 5.54; found: C, 67.63; H, 4.57; N, 5.58; IR (KBr; cm⁻¹); 3242, ν (NH); 1657, ν (C = O); 1587, ν (HC = N); 1480, 1436, 696, 518, ν (PPh₃); UV-Vis (CH₂Cl₂) λ_{max} (nm)(ε x10³, M⁻¹ cm⁻¹): 263 (16.92), 292 (9.44), 368 (2.80); ¹H NMR (CDCl₃; 300 MHz): δ 8.32 (s, 1H, HC = N), δ 10.34 (s, N-NHCO), δ 8.62 (s, C₆H₅CONH), δ 6.67–7.88 (m, phenyl).

Synthesis of $[Cu(L)(PPh_3)_2]ClO_4$ (2)

Complex 2 was prepared by a procedure similar to that used for the preparation of 1 except that CuCl was replaced by $[Cu(CH_3CN)_4]ClO_4$ (0.3335 g, 1 mmol).

Yield: 81 %; Elemental analyses (C, H, N, wt%) Anal. Calc. for C₅₇H₄₆CuN₄O₈P₂Cl: C,63.63; H, 4.31, N, 5.21; found: C, 63.60; H, 4.28; N, 5.23; IR (KBr; cm⁻¹); 3243, ν (NH); 1661, ν (C = O); 1593, ν (HC = N); 1481, 1436, 697, 518, ν (PPh₃); 1095, 621, ν (ClO₄); UV-Vis (CH₂Cl₂) λ_{max} (nm) ($\varepsilon \times 10^3$, M^{-1} cm⁻¹): 267 (22.85), 298 (9.15), 374 (1.78); ¹H NMR (CDCl₃; 300 MHz): δ 8.34 (s, 1H, HC = N), δ 10.31 (s, N-NHCO), δ 8.68 (s, C₆H₅CONH), δ 6.65–7.89 (m, phenyl).

Synthesis of [Cu(L)(PPh₃)₂]BF₄ (3)

Complex **3** was prepared by a procedure similar to that used for the preparation of **1** except that CuCl was replaced by $[Cu(CH_3CN)_4]BF_4$ (0.3205 g, 1 mmol).

Yield: 80 %; Elemental analyses (C, H, N, wt%) Anal. Calc. for C₅₇H₄₆CuN₄O₄F₄BP₂: C,64.39; H, 4.36, N, 5.27; found: C, 64.33; H, 4.32; N, 5.30; IR (KBr; cm⁻¹); 3245, ν (NH); 1659, ν (C = O); 1589, ν (HC = N); 1480, 1436, 696, 518, ν (PPh₃); 1057, ν (BF₄); UV-Vis (CH₂Cl₂) λ_{max} (nm)(ϵ x10³, M⁻¹ cm⁻¹): 264 (20.86), 294 (7.53), 372 (1.02); ¹H NMR (CDCl₃; 300 MHz): δ 8.31 (s, 1H, HC = N), δ 10.36 (s, N-NHCO), δ 8.65 (s, C₆H₅CONH), δ 6.71–7.98 (m, phenyl).

Synthesis of $[Cu(L)(PPh_3)_2]PF_6$ (4)

Complex 4 was prepared by a procedure similar to that used for the preparation of 1 except that CuCl was replaced by $[Cu(CH_3CN)_4]PF_6$ (0.3799 g, 1 mmol).

Yield: 78 %; Elemental analyses (C, H, N, wt%) Anal. Calc. for C₅₇H₄₆CuN₄O₄P₃F₆: C,61.05; H, 4.13, N, 5.00; found: C, 60.98; H, 4.02; N, 5.09; IR (KBr; cm⁻¹); 3244, ν (NH); 1655, ν (C = O); 1588, ν (HC = N); 1481, 1436, 696, 519, ν (PPh₃); 842, 556, ν (PF₆); UV-Vis (CH₂Cl₂) λ_{max} (nm)($\epsilon \times 10^3$, M⁻¹ cm⁻¹): 262 (23.21), 298 (12.72), 377 (2.73); ¹H NMR (CDCl₃; 300 MHz): δ 8.32 (s, 1H, HC = N), δ 10.33 (s, N-NHCO), δ 8.63 (s, C₆H₅CONH), δ 6.71–7.92 (m, phenyl).

X-Ray Crystallography

A single crystal of $[Cu(L)(PPh_3)_2]ClO_4$ (2) suitable for X-ray analysis was obtained by slow evaporation of saturated solution of complex in dichloromethane. X-ray intensity data were collected on a Nonius Kappa CCD diffractometer with graphite-monochromatized MoK α radiation. The details of crystal data, data collection and the refinement are given in Table 1. The structure was solved by direct methods using the SIR 92 program and refined by using CRYSTAL 97 software [28]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms bonded to C were refined using a riding model and H atoms bonded to N were allowed to refine freely.

Results and Discussion

The synthetic route to the formation of complexes 1-4 is shown in Scheme 1. N-(2-{[(2E)-2-(4-nitrobenzylidenyl)

Table 1Crystallographic data and refinement parameters for
complex 2

Empirical formula	$C_{57}H_{46}ClCuN_4O_8P_2$		
Formula weight	1057.97		
Crystal system	Monoclinic		
Space group	C2/c		
a (Å)	42.8596(9)		
b (Å)	14.6207(3)		
c (Å)	36.4643(7)		
α (°)	90.00		
β (°)	115.3263(6)		
γ (°)	90.00		
V (A ³)	20,653.7(7)		
Z	16		
Density (g/cm ³)	1.384		
$\mu (M_0 K_{\alpha})(mm^{-1})$	0.71073		
F (000)	8896		
Temperature (K)	200		
θ minimum-maximum (deg)	3.0 to 27.5		
Data set [h, k, l]	-55/55,-18/18,-47/42		
Observed data	<i>I</i> > 2.0σ(I)		
Refinement	Full-matrix least-squares on F ²		
R ₁ , R ₁	0.0430, 0.0839		
$wR_{2,}wR_{2}$	0.0787, 0.1038		
Goodness-of-fit	0.951		

hydrazinyl]carbonyl}phenyl)benzamide (L) was synthesized by the reaction of N-[2(hydrazinocarbonyl)phenyl]benzamide with 4-nitrobenzaldehyde. The obtained spectral data, elemental analysis and mass spectra confirm the formation of L. The mononuclear copper(I) complexes 1-4 possessing L and phosphine ligands were prepared via two simple steps. The complexes $[Cu(L)(PPh_3)_2]X$ (X = Cl, ClO₄, BF₄ and PF₆) were firstly afforded by the treatment of [Cu(CH₃CN)₄]X $(X = Cl, ClO_4, BF_4 and PF_6)$ with two equivalent of PPh₃ then one equivalent of L was slowly added. All the complexes were microcrystalline solids that were soluble in common organic solvents like dichloromethane, chloroform, acetonitrile, methanol, ethanol etc. Elemental analyses (C, H and N) given in section 2 confirm the assigned composition of the complexes. At room temperature all the complexes are diamagnetic, which is characteristic of Cu(I) (d¹⁰).

Spectroscopic Properties

The IR spectrum of L exhibits a broad band at 3248 cm⁻¹ which is characteristic of a ν (NH) vibration. This band

remains unchanged in 1-4, providing strong evidence for noninvolvement of the NH proton [29]. Another characteristic band at 1686 cm⁻¹ in L is assigned to $\gamma(C = O)$ vibration shifted to lower frequency by $25-31 \text{ cm}^{-1}$ in 1-4 providing strong evidence of the involvement of a carbonyl oxygen in the complexation with copper(I) via its keto form [30]. A band at 1618 cm⁻¹ in the spectrum of free ligand L attributed to v(C = N) shifts to 1587–1593 cm⁻¹ upon complexation indicating azomethine nitrogen coordination. This was also confirmed by the appearance of a new band at \sim 530 cm⁻¹ in 1–4 due to ν (C-N). The spectra of all of the copper(I) complexes exhibit the expected bands due to the PPh₃ ligand at around 1480, 1436, 696, 518 cm⁻¹. The perchlorate complex **2** exhibit a broad band at 1095 cm⁻¹(v_3) and a strong band at 621 cm⁻¹ (v_4) which is devoid of any splitting suggesting that the ClO₄⁻ anion is not coordinated to the copper(I) [31]. A broad band at 1057 cm⁻¹ in complex 3 corresponds to presence of $BF_4^$ anion in the complex [32]. The presence of the PF_6^- anion in **4** is shown by medium intensity band at 842 cm^{-1} and 556 cm^{-1} [33].

The UV-visible absorption spectra of 1–4 in CH₂Cl₂ (10⁻⁴ M) at ambient temperature are depicted in Fig.1. The ligand L shows two absorptions at $\lambda_{max} \approx 259$ and 286 nm, attributed to the π - π * transitions within L. Complexes 1–4 exhibit multiple absorption peaks in the range 262–298 nm region most likely coming from ligand L and PPh₃. The red shift of the π - π * absorption of 1–4 is consistent with better conjugation of the ligands upon coordination, resulting in a smaller π - π * energy gap. In addition to the high energy absorptions, complexes 1–4 also display a comparatively weak low energy absorption at ca 368–377 nm which can most likely be assigned to metal to ligand charge transfer transitions from the d π orbital of the copper(I) center to the unoccupied π * orbital of the ligand L [34].

¹H NMR spectra of **1–4** have been measured in CDCl₃ at room temperature. The ¹H NMR spectrum of free ligand L displayed a singlet at δ 8.26 ppm which can be assigned to the J Fluoresc



Fig. 1 Uv-visible spectra of 1-4

imine (HC = N) proton. In the spectra of complexes 1–4, the signal of the imine proton is considerably deshielded and appears as a singlet at δ 8.31–8.34 ppm due to positive charge delocalization on the corresponding C-atom through resonance resulting from the coordination of the ligand [35]. The downfield shift of –N-NHCO signals in the ¹H NMR spectra of 1–4 indicates participation of the hydrazide >CO group with the metal ion and observed at δ 10.31–10.36 ppm. However, the broad multiplet observed in the range δ 6.65–7.98 ppm for 1–4 can be assigned to the phenyl protons of the phosphine ligand and the ring protons of **L**.

X-Ray Crystal Structure

The crystals of $[Cu(L)(PPh_3)_2]ClO_4$ (2) were grown by slow diffusion of diethyl ether into a solution of the complex in dichloromethane and structure was determined by X-ray crystallography. X-ray analysis reveals that the complex 2 crystallizes in monoclinic space group C2/c with two molecules per asymmetric unit (molecule A and B) showing some small



Scheme 1 Synthetic route of L and its copper(I) complexes

conformational differences. The molecular structure of **2** along with the atom numbering scheme is illustrated in Fig. 2 and selected bond lengths and bond angles are collected in Table 2.

Complex 2 contains discrete $[Cu(L)(PPh_3)_2]^+$ cation and perchlorate anion with highly distorted tetrahedral geometry around the copper(I) with CuNOP₂ coordination. Ligand L is bonded to the copper ion in a bidentate manner through azomethine nitrogen and carbonyl oxygen form a five membered chelate ring. The distorted four-coordinate geometry of copper(I) is completed by imine nitrogen atom and one carbonyl oxygen atom of L and phosphorous atoms of two triphenylphosphine groups. The largest deviation from the ideal tetrahedral geometry is arises from the restricted bite angle of the chelating ligand. The intra-ligand chelate angles O(1)-Cu(1)-N(4) in A and O(101)-Cu(2)-N(104) in B are much less than 109.4°, being 77.57(8) and 76.94(8)°, respectively. In contrast, the P(1)-Cu(1)-P(2) angle in A is 122.35(3)° and the P(3)-Cu(2)-P(4) angle in **B** is 123.22(3)° have opened up due to steric effects from the bulky PPh₃ ligands. The average distance for Cu-N (2.110 Å), Cu-O (2.171 Å) and Cu-P (2.262 Å) are comparable to those reported for [Cu(A)(PPh₃)₂]NO₃ (2.061, 2.127 and 2.254 Å) [36].

Torsion angles in the chelating ring and hydrazone group are listed in Table 3. The chelating ring Cu(1)-N(4)-N(3)-C(2) in **A** and Cu(2)-N(104)-N(103)-C(102) in **B** are near planar and the sums of the three N atom bond angles are 357.96° in A and 359.95° in B. The significant deviations from 120° for the angles about the N atom (A: Cu(1)-N(4)-N(3), $108.66(17)^{\circ}$; Cu(1)-N(4)-C(5), $136.8(2)^{\circ}$ and C(5)-N(4)-N(3), $112.5(2)^{\circ}$; B: Cu(2)-N(104)-N(103), $109.87(15)^{\circ}$; Cu(2)-N(104)-N(105), $136.38(18)^{\circ}$ and C(105)-N(104)-N(103), $113.7(2)^{\circ}$).

Electrochemistry

The electrochemical properties of 1–4 were examined by cyclic voltammetrically in 10^{-3} M CH₂Cl₂ solution in the potential range \pm 1.5 V verses SCE electrode and are presented in Table 4. The electrochemical potential of 1–4 were

Fig. 2 Single crystal X-ray diffraction structure of $[Cu(L)(PPh_3)_2]ClO_4(2)$

 Table 2
 Selected bond lengths (Å) and bond angles (°) for 2

Bond lengths		Bond Angles	
Cu(1)-P(1)	2.2363(8)	P(1)-Cu(1)-P(2)	122.35(3)
Cu(1)-P(2)	2.2800(8)	P(1)-Cu(1)-O(1)	114.16(6)
Cu(1)-O(1)	2.1818(18)	P(2)-Cu(1)-O(1)	101.04(6)
Cu(1)-N(4)	2.115(2)	P(1)-Cu(1)-N(4)	125.98(7)
Cu(2)-P(3)	2.2668(8)	P(2)-Cu(1)-N(4)	104.56(7)
Cu(2)-P(4)	2.2664(8)	O(1)-Cu(1)-N(4)	77.57(8)
Cu(2)-O(101)	2.1595(18)	P(3)-Cu(2)-P(4)	123.22(3)
Cu(2)-N(104)	2.105(2)	P(3)-Cu(2)-O(101)	106.89(6)
		P(4)-Cu(2)-O(101)	105.30(6)
		P(3)-Cu(2)-N(104)	116.71(6)
		P(4)-Cu(2)-N(104)	115.36(6)
		O(101)-Cu(2)-N(104)	76.94(8)

characterized by a well defined redox process in the positive potential side. Complexes 1–4 display oxidative response at 0.672–0.688 V (E_{pa}) which is attributed to Cu(I)/Cu(II) oxidation. The potential appearing in the range 0.536–0.548 V (E_{pc}) is associated with reduction of Cu(II) to Cu(I). A quasireversible character is observed for all complexes with the values of ΔE_p ($\Delta E_p = E_{pa}-E_{pc}$) ranging from 136 to 140 mV under the conditions of the measurements.

Thermal Studies

In order to understand the thermal stability of the complexes, thermogravimetric (TG) studies of **1**, **3** and **4** were carried out between 25 and 800 °C under a nitrogen atmosphere. The perchlorate complex **2** is potentially explosive and hence not studied for safety reason. Complexes **1**, **3** and **4** showed two decomposition stages. The first decomposition stage takes place in the region 166–428(**1**), 172–431(**3**) and 168–428°(**4**) corresponding to mass loss of 50.23, 51.02 and 51.26 %, respectively and is attributed to the decomposition of coordinated triphenylphosphine (theoretical mass loss 51.12 % (**1**), 51.86 % (**3**) and 52.01 % (**4**)). The DTA curve gives exothermic peaks at 187° for **1**, 186° for **3**



Table 3 Torsion angles for chelating ring

Cu(1)-O(1)-C(2)-N(3)	12.2(4)
Cu(1)-N(4)-N(3)-C(2)	-4.6(4)
O(1)-C(2)-N(3)-N(4)	-5.5(5)
O(1)-Cu(1)-N(4)-N(3)	7.6(2)
N(4)-Cu(1)-O(1)-C(2)	10.8(2)
Cu(2)-O(101)-C(102)-N(103)	-11.8(4)
Cu(2)-N(104)-N(103)-C(102)	-4.6(4)
O(101)-C(102)-N(103)-N(104)	11.6(5)
O(101)-Cu(2)-N(104)-N(103)	1.0(2)
N(104)-Cu(2)-O(101)-C(102)	6.8(2)

and 189° for 4. The second stage shows further loss of weight from the range 428–656°, 431–658° and 428–662° along with strong exothermic DTA peaks at 328, 321 and 324 °C accompanied by a mass loss of 36.24 (1), 37.28 (3), 37.92 % (4) attributed to the decomposition of ligand L leaving CuCl, CuBF₄ and CuPF₆ as the final residue (theoretical mass loss 37.02, 37.48 and 38.15 %).

Fluorescence Spectral Studies

The fluorescence emission properties of L and complexes 1-4 have been investigated at room temperature in CH₂Cl₂ solution (10^{-4} M) and the data are displayed in Table 5. The ligand L exhibits an emission in the blue region centered at $\lambda_{\text{max}} = 428 \text{ nm}$ with an excitation maximum at 312 nm attributed to the fluorescence emission stemming from a ligandcentered π - π * transition. In contrast, complexes 1–4 show steady state marked differences in emission behavior in dichloromethane solution. As shown in Fig. 3, the spectra of 1-4 exhibit a broad emission profile in degassed CH₂Cl₂ at room temperature with λ_{max} at 470–491 nm upon excitation at 315-318 nm. Thus the fluorescence emission observed in 1-4 can be attributed to an intra-ligand charge transition (ILCT), a ligand to ligand charge transfer transition (LLCT) or mixture of both. The enhancement of fluorescence efficiency in all the complexes can be attributed to coordination of the ligands to copper(I) ion which effectively increases the rigidity of the ligands and reduced the loss of energy via radiation less

Table 4 Electrochemical data for copper(I) complexes (1-4)

Complex	E _{pa} (V)	E _{pc} (V)	$\Delta E_{p} (mV)$	$E_{1/2}(V)$
1	0.688	0.548	140	0.618
2	0.672	0.536	136	0.604
3	0.676	0.539	137	0.607
4	0.683	0.544	139	0.613

Supporting electrolyte: *n*-Bu₄NClO₄ (0.05 M); complex: 0.001 M; solvent: CH₂Cl₂; $E_{1/2} = \frac{1}{2}(E_{pa} + E_{pc})$; scan rate: 100 mVs⁻¹

Table 5Emission data of 1–4 in CH_2Cl_2 solution (10⁻⁴ M)

complex	λ_{ex} (nm)	$\lambda_{em}(nm)$	φ	τ (ns)	$K_r(s^{-1}/10^7)$	$K_{nr}(s^{-1}/10^9)$
1	318	470	0.072	3.19	2.250	0.290
2	315	482	0.085	3.39	2.507	0.269
3	316	475	0.078	3.41	2.280	0.271
4	317	491	0.091	3.42	2.660	0.265

thermal vibration decay [37]. There is a significant increase in the emission energy as well as the emission wavelength of 1–4 as size of the counter anion increases in the sequence $\text{Cl BF}_4 \leq \text{ClO}_4 \text{ PF}_6$ as their counter anion [38].

The fluorescence quantum yields (ϕ) of the complexes were determined by using quinine sulphate as a reference with known ϕ_R of 0.52 and appeared at 0.072–0.091 (Table 5). The area of the emission spectrum was integrated using the software available on the instrument and the quantum yields were calculated according to the following equation.

$$\frac{\phi_S}{\phi_R} = \frac{[A_S]}{[A_R]} X \frac{\left[(Abs)_R\right]}{\left[(Abs)_S\right]} X \frac{\left[\eta_S^2\right]}{[\eta_R^2]}$$

Here ϕ_S and ϕ_R are the fluorescence quantum yield of the sample and reference, respectively. A_S and A_R are the areas 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 and η_s and η_R are the values of refractive index for the respective solvent used for the sample and reference. The results obtained are in good agreement with those values reported in the literature [39]. The life time data of the complexes were obtained upon excitation at 320 nm and are summarized in Table 5. The observed decay of the complexes



Fig. 3 Emission spectra of 1-4

fit well with single exponential decay. The average lifetime of 1-4 follow the same sequence described above with respect to the increase in the size of the counter anion in the complexes. These results could be attributed to red shifted emission and decreased emission intensity in the complexes [40].

Conclusions

In conclusion, a series of copper(I) complexes featuring N-(2-{[(2E)-2-(4-nitrobenzylidenyl)hydrazinyl] carbonyl} phenyl)benzamide and triphenylphosphine have been prepared and characterized. It has been demonstrated that the ligand L is coordinated to copper(I) in its keto form by involvement of azomethine nitrogen and carbonyl oxygen in coordination. Complex 2 crystallizes in monoclinic space group C2/c with two molecules per asymmetric unit and assume distorted tetrahedral geometry around copper(I). Quasireversible redox behavior is observed for all complexes corresponding to a Cu(I)/Cu(II) couple. All complexes exhibit blue-green emission as a result of the fluorescence from intraligand charge transitions (ILCT), ligand to ligand charge transfer transitions (LLCT) or mixture of both. As the size of the counter anion increases a marked effect on the quantum efficiency (ϕ) and the lifetime decay (τ) of the complexes is observed.

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