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Synthesis and spectral studies of copper complexes using a N-octylated bis benzimidazole diamide ligand

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ABSTRACT

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Keywords: Bis benzimidazole diamide Copper(II) complexes Fluorescence quenching Monomeric Cu(II) and Cu(I) complexes bound to a tetradentate bis-benzimidazole diamide ligand N,N'-bis(N-octyl benzimidazolyl-2yl)(methyl)pentane diamide (O-GBGA) have been isolated and characterized. X-Band EPR spectra of the copper(II) complexes in CH₂Cl₂ were recorded in a frozen solution as solvent at liquid nitrogen temperature. Solution spectra typically indicate a $d_{x^2-y^2}$ ground state ($g_{\parallel} > g_{\perp} > 2.0023$) and show less than four nuclear hyperfine lines with broadening of g_{\perp} line in some cases, thus indicating distorted tetragonal geometry. One of the copper(II) complexes shows a five line N-SHF structure (16 ± 1 G) implying the binding of imine nitrogen of the benzimidazole to copper ion. α^2 ranges from 0.57–0.97 indicating considerable amount of covalent character in Cu–L bond. Anodic shifts in $E_{1/2}$ values indicate the retention of anion in the coordination sphere of Cu(II), $E_{1/2}$ values becoming anodic in the order C₆H₅COO⁻ < SCN⁻ < Cl⁻. The fluorescence quantum yield of complexes was found to be lower than that of the ligand O-GBGA ($\Phi = 0.029$) and the relative fluorescence data reveals that fluorescence of such compounds could distinguish between small and large anions.

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1. Introduction

Copper in metalloproteins acquires various coordination numbers and geometries [1,2]. Their redox properties are greatly affected by the nature of donor atoms, geometry and flexibility of the chelating ligands. Protein constraints are known to confer distorted geometries upon copper(II). Thus it is of interest to investigate model compound structures with imidazole and benzimidazole bound ligands, since the incorporation of bulky benzimidazole moieties, apart from mimicking the imidazole function in proteins, causes steric crowding and induces unusual coordination geometries [3].

Imidazole, pyrazole and benzimidazole amide ligands have been reported to afford peptidic Cu(II) complexes [4–12]. The present study reports the synthesis and spectral studies of copper(II) complexes with a new ligand N,N'-bis(N-octyl benzimidazolyl-2 methyl)pentane diamide (O-GBGA).

2. Experimental

2.1. Physical measurements

Elemental analyses were obtained from USIC, Delhi University, Delhi, INDIA.

Electronic spectra were recorded on a Shimadzu 1601 spectrophotometer.

IR spectra were recorded in solid state as KBr Pellets on a Perkin-Elmer FTIR-2000 spectrometer the range of 400–4000 cm⁻¹.

Cyclic-voltametric measurements were carried out using a BAS CV 50W electrochemical analyzing system. Cyclic-voltamograms of all the complexes were recorded in (2:8) DMSO:Acetonitrile solutions with 0.1 M tert-butyl ammonium perchlorate (TBAP) as supporting electrolyte. A three-electrode configuration composed of Pt-disk working electrode (3.1 mm² area), a Pt-wire counter electrode, and a Ag/AgCl reference electrode was used for the measurements. The reversible one-electron Fc⁺/Fc couple in the above solvent system has an $E_{1/2}$ of 0.487 versus Ag/AgCl electrode.

¹H NMR spectra were recorded on a 300 MHz BRUKER-spin instrument, at the Department of Chemistry, University of Delhi, India. AAS studies were carried out on Perkin-Elmer aanalyst-200 spectrophotometer at the Department of Chemistry, University of Delhi, India. Mass spectral studies were carried out on LCT Micro mass at the Department of Chemistry, University of Delhi, India. X-Band EPR spectra were recorded on a BRUKER-Spectrospin with

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Fig. 1. Tentative structures of the [Cu(O-GBGA)Cl₂].

a variable temperature liquid Nitrogen cryostat at 120 K at IIT, Kanpur, India.

Fluorescence studies were carried out on FL3-11, Fluorolog-3 spectro fluorometer at IIT, New Delhi.

2.2. Synthesis of ligand and complexes

2.2.1. Synthesis of the ligands

2.2.1.1. N,N'-bis(benzimidazolyl-2yl)(methyl)pentane diamide (GBGA). This ligand was synthesized using a procedure reported earlier [13]. The product was characterized by ¹H NMR spectra.

¹H NMR (δ ppm, d₆-DMSO): 1.84–1.80 (q, 2H), 2.25–2.20 (t, 4H), 4.5 (d, 4H), 7.1–7.4 (m, 8H), 9.11 (t, 2H), 12.30 (s, 2H).

2.2.1.2. N, N'-bis(N-octyl benzimidazolyl-2-yl)(methyl)pentane diamide (O-GBGA). N-octylation of GBGA to prepare O-GBGA was carried out as earlier [13]. GBGA (500 mg) was suspended in 20 ml of dry DMF and was stirred with dry K₂CO₃ (350 mg) for 4–5 h on a water bath at a temperature of 70–75 °C. Octyl bromide (0.44 ml) was added to the turbid solution and was allowed to stir for next 72 h on a water bath at a temperature of 70–75 °C. Subsequently the solvent was stripped off on a rotary evaporator and the residue was extracted with chloroform. The insoluble part was discarded. A white precipitate deposited along the sides of the beaker on the addition of hexane to the above chloroform filtrate. This was filtered and dried on anhydrous CaCl₂. This was recrystalized with hot methanol and analyzed for the composition $(C_{37}H_{54}N_6O_2)$

Yield: 250 mg, mp, 130 °C.

CHN analysis: found (calcd): C: 71.5 (72.3%); H: 9.0 (8.8%); N: 13.6 (13.7%).

IR data (ν /cm⁻¹): 3284 (ν _{NH} amide), 1642 amide I (ν _{C=0}), 1550 amide II (ν _{C=N} amide), 1473 (ν _{C=N-C=C} benzimidazole stretching).

NMR data (δ ppm) (CDCl₃): 11.26 (t, 2H), 7.59–7.25 (m, 8H), 4.78–4.76 (d, 4H), 4.12–4.10 (t, 4H), 2.43 (t, 4H), 2.08 (quin, 2H), 1.80 (quin, 4H), 1.32–1.24 (s, 20H), 0.86 (t, 6H).

UV data [λ_{max} (nm), (log ε) in CH₂Cl₂]: 284 (3.9), 276 (3.8), 252 (3.5).

2.2.1.3. Synthesis of the complex $[Cu(O-GBGA)Cl_2]$. To a methanolic solution of $CuCl_2 \cdot 2H_2O(0.48 \text{ mmol})(5 \text{ ml})$ was added a methanolic solution of the ligand O-GBGA (0.48 mmol) (10 ml) The resulting green coloured solution was stirred for 30 min, after which the volume was reduced on a water bath. The parrot-green product obtained was washed with small amount of methanol (4–5 ml) and air dried. The powdered compound was recrystallised by dissolv-

ing in warm methanol and allowed to cool slowly. The recrystallised product was analyzed for the composition CuC₃₇H₅₄N₆O₂·Cl₂. Yield: (50%).

CHN analysis: found (calcd): C: 58.1 (59.1); H: 8.0 (7.2); N: 11.0 (11.2); Cu: 8.12 (8.49).

UV–vis [λ_{max} (nm, log ε) in 2:8 DMSO:Acetonitrile]: 274 (4.09), 281 (4.06), 750 (2.40). $E_{1/2}$ versus Ag/AgCl: +0.53 (V).

We have earlier reported single crystal structures for a number of Cu(II) complexes with similar bis-benzimidazole diamide ligands that show clear evidence of the binding of this class of ligands through the amide carbonyl rather than amide NH [11–14]. Further in the synthetic procedure no base was employed so as to deprotonate the amide NH as has been reported for amides that bind through amide NH rather than amide carbonyl [15]. A tentative structure of complex is given in Fig. 1. The mass spectrum is shown in Fig. 1.1 (Supplementary data). m/z = 749.3.

2.2.1.4. Synthesis of the complex [Cu(O-GBGA)(CH₃COO)₂]. A dilute methanolic solution of aqueous NaOH was added drop wise to a 5 ml methanolic solution of CuCl₂·2H₂O (0.48 mmol) till the formation of a light-green precipitate was completed. This solution was centrifuged and the filtrate was discarded. The precipitate was washed 4 times with methanol. To this slurry, a very dilute solution of acetic acid (CH₃COOH, in methanol) was added drop wise till all precipitate dissolves. This was centrifuged and the filtrate was added immediately to a methanolic solution of the ligand (O-GBGA) (0.48 mmol). This solution was stirred for 2 h on a water bath at 40 °C. Reduction in its volume by evaporation and leaving it in the freezer for 30 min resulted in a bluish-green product which was dried in air. This product was recrystallised as before by dissolving in minimum amount of hot methanol, and cooling. A pure dark blue product was obtained which was air dried and analyzed for the composition of $CuC_{37}H_{54}N_6O_2$ (CH₃COO)₂. A direct reaction with the copper(II) acetate salt with the ligand gave an identical product, however the yield was lower in comparison to the modified procedure adopted in the present case.

Yield: (55%).

CHN analysis: found (calcd): C: 61.6 (61.8); H: 8.3 (7.5); N: 11.0 (10.5); Cu: 8.01 (7.98).

UV data: $[\lambda_{max} (nm, \log \varepsilon) in 2:8 DMSO: Acetonitrile]: 274(3.22), 281 (4.04), 650 (2.33).$

2.2.1.5. Synthesis of the complex $Cu[(O-GBGA)(C_6H_5COO)_2]$. This complex was synthesized by the method as described for the acetato complex, except that in this case benzoic acid was taken in place of acetic acid. This was done as no analogous copper(II)

benzoate salt was available. The pale green product obtained was analyzed for the composition $CuC_{37}H_{54}N_6O_2 \cdot (C_6H_5COO)_2 \cdot 2H_2O$. Yield: (59%).

CHN analysis: found (calcd): C: 63.4 (64.0); H: 7.9 (7.1); N: 8.0 (8.8); Cu: 6.26 (6.65).

UV data: $[\lambda_{max} (nm, \log \varepsilon) in 2:8 DMSO: Acetonitrile]: 274 (3.75), 282 (4.02), 755 (2.58).$

 $E_{1/2}$ versus Ag/AgCl: +0.46 (V). m/z = 919.6.

2.2.1.6. Synthesis of the complex $[Cu^{I}(O-GBGA)(SCN)]$. For the preparation of this complex, CuCl₂·2H₂O was first converted to Cu(SCN)₂. This was done since a copper(II) salt with thiocyanate was unavailable. A solution of KSCN in MeOH was added dropwise to the solution of CuCl₂·2H₂O (0.48 mmol) in 5 ml MeOH, till there was no further precipitation. After centrifugation, the centrifugate, a brown solution, was added immediately to the solution of ligand O-GBGA (0.48 mmol) in 15 ml methanol. A green precipitate was obtained after 1/2 h of slow stirring of solution-mixture in a septum sealed three neck flask. A solution of quinol (0.48 mmol) in methanol (10 ml) was then transferred under nitrogen, via a double end needle, to the copper(II) complex solution. Immediate colour change from peacock green to pale yellow was observed. Stirring for 10 min resulted in a white solid that was filtered off, washed with methanol and air-dried. This compound was analyzed for the composition $CuC_{37}H_{54}N_6O_2$ ·SCN·2H₂O.

Yield: (46%).

CHN analysis: found (calcd): C: 58.0 (59.1); H: 8.0 (7.5); N: 12.5 (12.7); S: 4.0 (4.1); Cu: 8.32 (8.23).

UV–vis [λ_{max} (nm, log ε) in 2:8 DMSO:Acetonitrile]: 272 (4.35), 282 (4.30), 293 (3.80).

 $E_{1/2}$ versus Ag/AgCl: +0.50 (V). The oxidation state of copper was confirmed by ¹H NMR spectra.

3. Results and discussion

3.1. Electronic spectroscopy

The electronic spectra of the copper(II) complexes were recorded in mixed DMSO/Acetonitrile and DMF/Acetonitrile (2:8), solvent system. Two peaks in the range 270–285 nm are observed for all the complexes which have been assigned to intraligand π – π * transition of benzimidazole moiety in their respective ligands [16]. The bands show enhanced absorptions as indicated by their extinction coefficients. A band around 293 nm is assigned to the charge transfer band from ligand to metal for the Cu(O-GBGA)(SCN) complex.

The copper(II) complexes exhibit a broad d-d band in the region 600–800 nm, characteristic of tetragonal geometry. This broad band is obtained due to the overlapping transitions and $d_{xy} \rightarrow d_{x_2-y_2}$. The difference in absorption band position is often attributed to the ligand field splitting of the coordinated ligand. The decrease in energy of the absorption maxima on going from CH₃COO⁻ > Cl⁻ ~ C₆H₅COO⁻ in O-GBGA complexes can be attributed to a decrease of the in-plane LFS, which reflects different degrees of distortions of copper(II) ion bound to the ligand.

3.2. EPR spectra

X-Band EPR spectra of the copper(II) complexes were recorded in a frozen solution in CH₂Cl₂ as solvent at liquid nitrogen temperature (Fig. 2 and Table 1). Solution spectra typically indicate a $d_{x^2-y^2}$ ground state ($g_{\parallel} > g_{\perp} > 2.0023$). Solution state spectra in the complexes show less than four lines and a broadening of g_{\perp} line in some cases, thus indicating severely distorted tetragonal geometry.

Broadening of g_{\perp} indicates lowering in symmetry that manifest itself through rhombic splitting [11,12]. The A_{\parallel} and g_{\parallel} values for the



Fig. 2. X-Band EPR spectra of $[Cu(O-GBGA)Cl_2]$ (1), $[Cu(O-GBGA)(C_6H_5COO)_2]$ (2) and $[Cu(O-GBGA)(CH_3COO)_2]$ (3) in CH_2Cl_2 at microwave frequency 9.448 GHz and receiver gain 10³.

Table 1

X-Band EPR data of copper(II) complexes of the ligand (O-GBGA), at 120 K.

Complex	$g_{ }$	<i>g</i> ($A_{ }$	α^2	$(g_{ }/A_{ })/10^{-4}$
$[Cu(O-GBGA)(NO_3)_2]$ [13]	2.31	2.10	130	0.62	177
$[Cu(O-GBGA)Cl_2]$	2.30	2.10	143	0.59	160
$[Cu(O-GBGA)(C_6H_5OO)_2]$	2.29	2.05	166	0.57	137
$[Cu(O-GBGA)(CH_2COO)_2]$	2.42	2.13	181	0.90	133

complexes do not lie on the Peisach Blumberg Plots of $A_{||}$ versus $g_{||}$ for two nitrogen and two oxygen in structural plane and suggests a distortion of the equatorial plane. The values of hyperfine coupling constant $A_{||}$ are quite low in comparison to the normal range found for other copper(II) complexes, implying a marked tetrahedral distortion of the tetragonal site [17]. The factor $g_{||}/A_{||}$ also reflects the distortion of coordination geometry. Higher the value of this factor, greater is the distortion. This is because when the geometry is no longer planar, repulsion between the unpaired electron in the $d_{x^2-y^2}$ orbital and ligand electron pair decreases. As a result, this unpaired electron can now be delocalized on the ligand framework to a greater extent thus reducing coupling with the copper nucleus and lowering the $A_{||}$ value.

Further no nitrogen super hyperfine splitting could be observed, implying non-planarity of the complexes, except in case of [Cu(O-GBGA)(C₆H₅OO)₂] complex, where blow up of g_{\perp} peak shows very weak, five line structure of 16 ± 1 G (Fig. 2), indicating the N-

able 2
able 2

IR spectral studies of the Cu(II) and Cu(I) complexes with ligand N,N'-bis(2-benzimidazolylethyl)hexanediamide (O-GBGA).

Assignments (KBr Pellets)	$[Cu(O-GBGA)Cl_2]$	[Cu(O-GBGA)(SCN)]	$[Cu(O-GBGA)(C_6H_5OO)_2]$	$[Cu(O-GBGA)(CH_3COO)_2]$
v _{NH} amide	3171	3205	3265	3183
gv _{C=0} amide I	1623	1656	1631	1640
v _{C-N} amide II	1550	1541	1550	1545
$\nu_{C=C-N=C-}$ gp.	1455	1445	1455	1450
v_{special} for anions		2077	1600	1330

KBr Pellets (cm⁻¹).

super hyperfine structure, due to two equivalent benzimidazole N-atoms coordinated to the copper(II) nucleus, such N-super hyper line structure has been reported by us for copper(II) complexes with similar benzimidazole based ligands [13,17]. $g_{\parallel}/A_{\parallel}$ follows the order CH₃COO⁻ ~ C₆H₅COO⁻ < Cl⁻ for O-GBGA series indicating that distortion in coordination geometry is least for acetate and greatest in the chloro complex. The covalency factor α^2 has been calculated (Table 1) using the relationship.

$$g_{||} = 2.0023 - \frac{8\lambda lpha^2}{\Delta XY}$$

where λ is the spin orbit coupling constant for copper(II) and ΔXY is the *d*-*d* band energy in cm⁻¹ for the respective copper(II) complex [18]. α^2 is a function whose numerical value depends on the nature of copper–ligand bond and decreases with increasing covalency of Cu–L bond. The minimum theoretical value of α^2 is 0.5 and maximum is 1.0.

For the series of complexes obtained from O-GBGA ligand, α^2 ranges from 0.59–0.90 indicating considerable amount of covalent character in Cu–L bond. It is interesting to note that the chloro complex in this series is relatively more covalent, while the acetato complex is more ionic for this series.

3.3. Cyclic voltammetry

All the complexes display a quasi reversible redox wave due to Cu(II)/Cu(I) process. Anodic shifts in $E_{1/2}$ values indicate the retention of anion in the coordination sphere of Cu(II). $E_{1/2}$ values becoming anodic in the order C₆H₅COO⁻ < SCN⁻ < Cl⁻ for the O-GBGA series. The CH₃COO⁻ bound complex shows an irreversible anodic wave at 0.57 V versus Ag/AgCl.

3.4. ¹H NMR study of $[Cu^{I}(O-GBGA)(SCN)]$

The ¹H NMR spectrum of the free ligand O-GBGA shows signals for aliphatic and aromatic protons with theoretically predicted splittings. A signal is observed between 11.26 ppm corresponding to N–H amide proton; while multiplets in the range 7.2–7.5 ppm arise due to the benzimidazole ring protons. The linker $-CH_2$ – protons are found at 2.0 and 4.1 ppm for the ligand. The $-CH_2$ – group adjacent to the benzimidazole ring gives rise to a doublet between 4.7 ppm due to coupling with the adjacent amide NH protons. The methylene $-CH_2$ – and the methyl $-CH_3$ of the octyl chain are observed at 2.4, 1.8, 1.2, and 0.8 ppm, respectively [13].

In the ¹H NMR spectrum of the complex synthesized using SCN⁻ as the anion, shifted signals were observed with the loss of splitting. The central linker $-CH_2$ protons and those of the octyl chain show a very slight shifting. While some of the ¹H signals were found to be downfield shifted as compared to the free ligand O-GBGA, these include the benzimidazole ring protons which appear at 7.9 ppm instead of 7.5 ppm and the methylene protons that appear at 4.3 ppm instead of 4.1 ppm. The amide NH proton is upfield shifted at 9.2 ppm instead of 11.2 ppm. The $-CH_2$ - group adjacent to the benzimidazole ring gives rise to a doublet at 4.7 ppm due to coupling with the adjacent amide NH protons. The presence of amide NH protons proves that the copper ion does not coordi-

nate through the amide NH. Loss of splitting, downfield shifting and slight broadening confirms that copper in this complex exists in the +1 oxidation state.

3.5. IR spectral studies

In all the complexes, IR bands due to benzimidazole NH and amide NH are shifted considerably indicating the involvement of these groups in hydrogen bonding either with the solvent molecules or with the exogenous anionic ligand in the complexes [11].

Shift in amide I band, due to C=O group and increase/decrease in amide II band, due to C-N group, in the amide are indicative of the coordination of the ligand through carbonyl oxygen in the complexes (Table 2) [11–13,17].

A broad band in the region 3300–3500 cm⁻¹ in all the complexes indicates the presence of water molecule or O–H stretching due to H-bonding with the solvent. The presence of anions in the respective complex is justified by the presence of strong IR bands at 2077 cm⁻¹ (ν_{SCN} stretch), 846 cm⁻¹ (ν_{C-N} stretch). This shows coordination group through N atom of thiocynate group. Bands at 1600 ($\nu_{C_6H_5COO-}$), 1330 cm⁻¹ (ν_{CH_3COO-}) are assigned to unidentate mode of binding of the respective anions [19].

3.5.1. Fluorescence studies

The fluorescence spectra of the O-GBGA and its copper(II/I) complexes are shown in Fig. 3. Quantum yields φ (Table 3) were calculated by comparison of the spectra with that of anthracene (φ = 0.292) taking the area under the total emission.



Fig. 3. Fluorescence spectra of ligand (5) and [Cu(O-GBGA)Cl₂] (1), [Cu(O-GBGA)(NO₃)₂] (2), [Cu(O-GBGA)(C₆H₅COO)₂] (3), [Cu(O-GBGA)(C₆H₅COO)₂] (4) in concentration of 7×10^{-6} M in HPLC grade CH₂Cl₂.

Table 3

Fluorescence spectra of copper(II) complexes with O-GBGA in concentration of $7.0\times 10^{-6}\,M$ in HPLC grade $CH_2Cl_2.$

Complexes Qu	antum yield (photon)
O-GBGA 0.0)29
[Cu(O-GBGA)(CH ₃ COO) ₂] 0.0)10
[Cu(O-GBGA)Cl ₂] 0.0)22
[Cu(O-GBGA)(NO ₃) ₂] 0.0)21
$[Cu(O-GBGA)(C_6H_5COO)_2] 0.0$)12

The fluorescence spectrum of 7 µM solution in dichloromethane for O-GBGA shows two groups of bands, one group (F1) arising between 350 and 385 nm, while the other arising between 400 and 465 nm (F2). The short wave length fluorescence bands within (F1) are found to be red shifted with respect to simple benzimidazole and bis benzimidazole type ligands [20,21]. The fluorescence quantum yield of the present ligating system is similar to that reported for bis benzimidazole type ligand but quite higher than for some of the nitrogen containing fluorophores [22], implying that the lone pair of the benzimidazole nitrogen is only weakly involved in photo induced electron transfer (PET) to the aromatic fluorophore. The fluorescence spectra of the copper(II) complexes of O-GBGA show only very slight shift in the λ_{max} of the bands in 350–465 nm region, as compared to the ligand. However, the total area under the curve between these wavelength regions does change. This change is reflected in the quantum yields as reported in Table 3. The quantum yields have been calculated by utilizing the formula:

$$\Phi = 0.292 \frac{\text{area}_{\text{comp}}}{\text{area}_{\text{anth}}} \frac{\varepsilon_{\text{anth}}}{\varepsilon_{\text{comp}}}$$

where ε = extinction coefficient of the compound, while anth: anthracene.

The fluorescence quantum yields of complexes were found to be lower than that of the ligand O-GBGA. This indicates that all complexes quench the fluorescence of the parent ligand. However, some changes are observed which are assigned to the effect of the anion bound to the copper(II) complexes. Much larger quenching is observed for the acetate and benzoate bound complexes rather than the chloride complexes.

The relative fluorescence intensity change (σ) is given by:

$$\sigma = \frac{F_0 - F_0}{F_0}$$

where F_0 , fluorescence intensity of free ligand; F, fluorescence intensity of the complex.

The relative fluorescence intensity data reveals that for the larger anions like acetate and benzoate, value of σ is also larger (0.65, 0.58) while for smaller anions like chloride and nitrate σ relative is smaller (0.24, 0.27). This suggests that fluorescence of such compounds could distinguish between small and large anions.

4. Conclusion

New copper(II) complexes with a N-octylated bis benzimidazolyl ligand have been synthesized and characterized. IR spectral study confirms the binding of amide carbonyl rather than amide-NH a result supported by crystal data on similar bis-benzimidazolyl diamide ligands. EPR work suggests a highly distorted copper(II) geometry in solution state as evidenced by low A_{\parallel} values, further N-SHF structure on one of the complexes, implicates the binding of imine N-atoms of the benzimidazole, giving a N₂O₂ donor environment on copper(II). The ligand and its copper(II) complexes give fluorescence quantum yield which is higher than for some nitrogen containing fluorophores implying that the lone pair of the benzimidazole N-atom is only weakly involved in PET to the aromatic fluorophore. The relative fluorescence intensity change reveals that it is larger for larger anions like CH₃COO⁻ and C₆H₅COO⁻ while smaller for anions like Cl⁻ and NO₃⁻. Thus, fluorescence of these copper(II) compounds can distinguish between small and large anions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.11.033.

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