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# 1-(Pyridin-2-ylmethyl)-2-(3-(1-(pyridin-2-ylmethyl)benzimidazol-2-yl) propyl) benzimidazole and its copper(II) complex as a new fluorescent sensor for dopamine (4-(2-aminoethyl)benzene-1,2-diol)

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### ARTICLE INFO

Article history: Received 4 July 2012 Accepted 18 February 2013 Available online 24 February 2013

Keywords: Benzimidazole Copper complex Structure Fluorescent sensor

### ABSTRACT

A new ligand 1-(pyridin-2-ylmethyl)-2-(3-(1-(pyridin-2-ylmethyl)benzimidazol-2-yl) propyl) benzimidazole (**L**) and its Cu(II) complex (**1**) have been synthesized and characterized spectroscopically and structurally. The Cu(II) ion is coordinated by two nitrogen atoms of benzimidazole groups, two oxygen atoms of the nitrate anions and one oxygen atom of a water molecule forming distorted trigonal bipyramidal geometry. The ligand and its complex have been utilized as a fluorescent sensor for 4-(2-aminoethyl)benzene-1,2-diol. A plot of  $F_0/F - F_0$  vs 1/Conc (4-(2-aminoethyl)benzene-1,2-diol) at a selected wavelength of 306 nm with (**L**) that shows a straight line behavior, supports the validity of the assumption of 1:1 complex formation and the association constant of (**L**) with 4-(2-aminoethyl)benzene-1,2-diol is calculated to be 9868 M<sup>-1</sup>. Sensor (**L**) is found to be selective for 4-(2-aminoethyl)benzene-1,2-diol over aromatic amines, phenols, amino catechol (L-3,4-dihydroxyphenylalanine) and 4,6-ditertiarybutyl benzene-1,2-diol.

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The development and use of fluorescent chemosensors have increased over the recent years [1]. The ability of chemosensors to bind to neurotransmitters, in particular catecholamines has been of great interest. Catecholamines, such as 4-(2-aminoethyl)benzene-1,2-diol, 4-(1-hydroxy-2-(methylamino)ethyl)benzene-1,2-diol, 4-(2-amino-1hydroxyethyl)benzene-1,2-diol and L-3,4-dihydroxyphenylalanine are involved in a variety of central nervous system functions. The lowered concentration of 4-(2-aminoethyl)benzene-1,2-diol acting as a neurotransmitter in the brain is known to lead to several neurodegenerative diseases, like alzheimer, Wilson and Parkinson [2–4]. Besides the Tyrosinase mediated oxidation of L-3.4-dihydroxyphenylalanine [5] non enzymatic oxidation of 4-(2-aminoethyl)benzene-1,2-diol is reported to be accelerated by nteraction of transition metal ions [6]. Metal ion sensing has also been reported using new efficient chemosensors [7]. Recently Schiff-base ligand derivatives of neurotransmitter 4-(2-aminoethyl)benzene-1,2-diol, bearing an imidazole, methylimidazole or hydroxynaphthaldehyde units have been reported for the selective detection of  $Al^{3+}$  [8]. However there are only few reports regarding fluorescence sensing of neurotransmitters 4-(2aminoethyl)benzene-1,2-diol and L-3,4-dihydroxyphenylalanine [9–12].

A phenylboronic acid derivative of a well-known dye (Lucifer yellow) recognizes L-3,4-dihydroxyphenylalanine through a combination of reversible esterification, charge transfer, and electrostatic interactions. The selective recognition event is signaled by a drop in the emission intensity of the fluorescent chemosensor [10]. In a more recent

study Raymo presented a diazapyrene-based 4-(2-aminoethyl)benzene-1,2-diol chemosensor attached to silica particles [13] and glass and his coworker reported coumarin aldehyde as a selective chemosensor for 4-(2-aminoethyl)benzene-1,2-diol and 4-(2-amino-1-hydroxyethyl) benzene-1,2-diol [11]. Chemosensors, anthracene fluorophore bearing boronic acid and aldehyde group for 4-(2-aminoethyl)benzene-1,2-diol recognition have also been reported [9,12].

In the present paper, we have developed a new benzimidazole fluorophore 1-(pyridin-2-ylmethyl)-2-(3-(1-(pyridin-2-ylmethyl) benzimidazol-2-yl)propyl)benzimidazole (L) (Scheme 1) [14] and its Cu(II) complex (1) [15]. They have been characterized by single crystal X-ray crystallographic measurement [16]. The purpose of including the N-pyridyl group is to understand its impact on the fluorescence properties of the ligating moiety. Further modification of the steric properties of the ligand would also affect the geometry of the bound Cu(II) ion. The present ligating system has been utilized as a selective fluorescent chemosensor for 4-(2-aminoethyl) benzene-1, 2-diol.

All chemicals glutaric acid (Aldrich), benzene-1, 2-diamine, 2-(chloromethyl)pyridine and spectroscopic solvents were obtained from commercial sources and used without further purification. 2-(3-(benzimidazol-2-yl)propyl)benzimidazole (**GAB**) was prepared as described earlier [17,18].

<sup>1</sup>H NMR spectrum of the free ligand (L) [Fig. 1.1 Supplementary data] shows signal at 8.4 ppm and is assigned to the H's adjacent to the N atom of the pyridyl group. A singlet is also observed at 5.6 ppm which is assigned to the  $CH_2$  protons linked to pyridine ring. A triplet in the range 2.9–3.0 ppm and a quintet in the range 2.2–2.3 ppm are

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1-(pyridin-2-ylmethyl)-2-(3-(1-(pyridin-2-ylmethyl)benzimidazol-2-yl) propyl)benzimidazole

Scheme 1. Synthesis of 1-(pyridin-2-ylmethyl)-2-(3-(1-(pyridin-2ylmethyl)benzimidazol-2-yl)propyl)benzimidazole (L).

observed and are assigned to  $CH_2$  protons present in the aliphatic chain. Multiplets are observed in the range 7.1–7.8 ppm and are assigned to the protons of the benzimidazole ring and pyridine ring. <sup>13</sup>C NMR spectrum of the ligand [Fig. 1.2 Supplementary data] shows signals at 28 and 26 ppm and is assigned to methylene carbons of the aliphatic chain. Signals at 156.5 and 149 ppm are attributed to carbons adjacent to the N-atom of the pyridine ring. Benzene ring and pyridine ring carbons appeared in the range (119–124 ppm) and (137–144 ppm) [19].

The free ligand (**L**) has characteristic IR bands at 1616 and 1463 cm<sup>1</sup>. These are assigned to pyridyl (mainly  $v_{C=N}$  stretch) and benzimidazole  $v_{C=N-C=C}$  stretching frequencies, respectively. Small shift upon complexation is attributed to the binding of imine nitrogen to copper(II). I.R data of ligand and its complex is being reported [14,15]. A broad band in the region 3350–470 cm<sup>-</sup> in the ligand and its complex is assigned to the  $v_{O-H}$  stretching vibrations. In the nitrate complex three bands at 1011, 1336 and 1435 cm<sup>-1</sup> are assigned to monodentate nitrate bound to copper(II), separation between the two highest peak is around 100 cm<sup>-1</sup> [20].

The electronic spectra of ligand (L) and the complex were recorded in HPLC grade DMF [14,15]. Three peaks in the range 265–285 nm are observed in the free ligand and its complex are assigned to the intraligand  $\pi$ – $\pi$ \* transition of benzimidazole and pyridyl moiety present in the ligating system. The Cu(II) complex (1) displays a broad d–d band at 800 nm assigned to the overlapping transition  $d_{xz,yz} \rightarrow d_{x^2-y^2}$  and  $d_{xy} \rightarrow d_{x^2-y^2}$ .

The cyclic voltammogram of the Cu(II) complex (**1**) was recorded in 3:2 DMSO:CH<sub>3</sub>CN with tert-butyl ammonium peroxide (TBAP) 0.1 M as supporting electrolyte. A three electrode configuration composed of Pt working electrode 3.1 mm<sup>2</sup> area, a Pt wire counter electrode, and

an Ag/AgNO<sub>3</sub> electrode reference electrode were used for the measurement. The reversible one electron Fc<sup>+</sup>/Fc couple in the above solvent system has an  $E_{1/2}$  of 59.5 mV vs. Ag/AgNO<sub>3</sub> electrode. The complex displays a quasi reversible redox waves due to the Cu(II)/Cu(I) reduction process with  $E_{1/2}$  value – 96.3 mV [Fig. 1.3 Supplementary data]. The  $E_{1/2}$  value of this complex is relatively more cathodic when compared to benzimidazole and diamide benzimidazole bound Cu(II) complexes [6d,21] indicating that this will not undergo any redox reaction with 4-(2-aminoethyl)benzene-1,2-diol. This is also revealed in the fluorescence titration of this complex with 4-(2-aminoethyl)benzene-1,2-diol where no new band is observed due to oxidation of 4-(2-aminoethyl) benzene-1,2-diol benzene-1,2-diol to quinone.

The X-band EPR spectra of Cu(II) complex (1) have been recorded in DMSO at liquid nitrogen temperature. The spectra typically indicates a  $d_{x^2-y^2}$  ground state ( $g_{\parallel} > g_{\perp} > 2.0024$ ). The  $g_{\parallel}$  and  $g_{\perp}$  are found to be ~2.29 and ~2.01 with an  $A_{\parallel}$  value of 128 G. The complex shows four  $g_{\parallel}$  components and a broadening of  $g_{\perp}$  component [Fig. 1.4 Supplementary data]. Such a broadening of the g<sub>1</sub> component is indicative of the lowered symmetry [22]. As fluorescence experiments were carried out in solution state, therefore it was important to find out if there are geometric changes of the copper(II) complex from the solid state to the solution state. EPR of the copper(II) complex was recorded for this purpose and indeed shows that there are changes in the geometry, the distorted trigonal bipyramidal geometry of the solid state changes to distorted six coordinate tetragonal geometry in DMF, as suggested by the  $g_{\parallel}$ ,  $g_{\perp}$  and  $A_{\parallel}$  parameters. Thus it is this tetragonal copper(II) species which is showing fluorescence emission spectra in the titration experiment carried out with 4-(2aminoethyl)benzene-1,2-diol.

The ORTEP diagram of 1-(pyridin-2-ylmethyl)-2-(3-(1-(pyridin-2-ylmethyl)benzimidazol-2-yl)propyl)benzimidazole (**L**) with atom numbering scheme is shown in (Fig. 1). A total of 19,709 reflections were measured, of which 4809 were unique and 2181 were considered as observed (I>2 $\sigma$  (I)]. It crystallizes in the monoclinic system with space group P21/n. All H atoms were positioned geometrically with C-H distances ranging from 0.95 to 0.99 Å. The ligand is bidentate with two benzimidazole N-donar atoms. The bond lengths of C–N imidazole are in the range 1.308–1.385 Å and bond angles N–C–N of imidazole ring are 110.6(3) and 111.5(3)° and are comparable to the similar ligand 1,3-bis(1-benzyl-1H-benzimidazol-2-yl)-2-oxapropane reported earlier with C–N imidazole bond lengths in the range 1.31–1.37 Å and N–C–N bond angles that are 113.39° and 113.75 [23].

The ORTEP diagram of Cu(II) complex (1) and atom numbering scheme is shown in (Fig. 2). The complex was dissolved in HPLC grade methanol, and slow evaporation at room temperature over a period of 48 h resulted in the formation of green needle shape crystal. A total of 21,455 reflections were measured, of which 5193 were unique and 3314 were considered as observed (I> $2\sigma$  (I)]. It crystallizes in the monoclinic system with space group P21/n. Cu(II) ion is penta-coordinated by two N atoms of benzimidazole (N1, N4), two oxygen atoms of nitrate group (02, 05) and O(1) atom of solvent molecule H<sub>2</sub>O. One uncoordinated methanol molecule is present in the molecular structure. The Cu–N bond distances of 2.279(2) Å (Cu-N1) and 2.0058(18) Å (Cu-N4) are in the range found for similar benzimidazole ligated compounds [24]. (Cu-O1), (Cu-O2) and (Cu-O5) bond distances are 1.9470(18), 1.9729(17) and 2.0110(15) Å. Bond angles C(17)-N(4)-Cu(1) and C(7)-N(1)-Cu(1) are 129.28(17)° and 129.25(16)°. In five co-ordinate systems the actual geometry of the complex can be described by a structural index parameter  $\tau$ . Five co-ordinate system such as (1) ideally square pyramidal geometry is associated with  $\alpha = \beta = 180^\circ$ , for A as the axial ligand ( $\beta$  is the greater of the basal angle BMC). For perfectly trigonal bipyramidal geometry  $\alpha$  becomes 120° and BMC the principal axis 180°. The penta co-ordination geometries can be characterized by the value of ( $\beta$ - $\alpha$ ) which is 0° for C<sub>4v</sub> and 60° for a D<sub>3 h</sub> co-ordination geometry. The geometric parameter  $\tau$  (Addison parameter) is thus defined as  $\tau = (\beta - \alpha)/60^\circ$ . According to this model, out of the equatorial ligands (A, D, E), A is chosen such that the Cu – A bond length is longer than the Cu - D/E and A should not be any one of the four donar atoms forming the two largest angles. Thus geometric parameter  $\tau$  is applicable to five co-ordinated structures as an index of the degree of trigonality within the structural continuum between trigonal bipyramidal ( $\tau$  = 1) and square pyramidal ( $\tau$  = 0).

$$\begin{array}{c} A \\ B \\ \hline \\ B \\ \hline \\ \\ E \\ D \end{array} \right) C$$
 (1)

The complex has  $\tau = 0.372$ , where  $\alpha$  is the angle between O5-Cu-N4 (156.97(8)°) and  $\beta$  is the angle between O2-Cu-O1 (179.34(9)°) indicating a highly distorted trigonal bipyramidal geometry. This type of distorted geometries are reported earlier with  $\tau = 0.39$  [25]. The equatorial bond angles deviates from the expected value of 120° N1-Cu (1)-O5=93.38(7)°, O5-Cu(1)-N4=156.97(8)° and N1-Cu (1)-N4=109.65(8)°. The deviation in equatorial bond angles suggests remarkable asymmetry within the trigonal plane. The sum of the equatorial bond angles is 360° indicating that Cu metal center resides in the equatorial plane.

The fluorescence spectra of the ligand 2-(3-(benzimidazol-2-yl) propyl)benzimidazole (GAB), 1-(pyridin-2-ylmethyl)-2-(3-(1-(pyridin-2-ylmethyl)benzimidazol-2-yl)propyl) benzimidazole (L) and its copper(II) complex (1) in DMF are shown in (Fig. 3). Quantum yield  $\Phi$  were calculated by comparison of the spectra with that of anthracene  $(\Phi = 0.292)$  taking the area under the total emission [26]. Emission spectra of (L) and its complex were recorded at slit width 5.0 but the intensity of the unsubstituted ligand (GAB) is out of the range at slit width 5.0, so emission spectrum is recorded at 2.5 slit width, still its intensity is higher than (L). This suggests that fluorescence intensity is quenched due to N-substitution of (GAB). The fluorescence spectra of the copper(II) complex (1) in DMF shows only a very slight shift in the emission spectra but the intensity of the complex is quenched as compared to the parent ligand showing complexation with imine nitrogens of the benzimidazole moiety. This change is reflected in the guantum yield. The fluorescence quantum yield of copper(II) complex (1) is found to be lower ( $\Phi = 0.02$ ) than that of the parent ligand ( $\Phi = 0.06$ ).



Fig. 1. Ortep diagram of ligand (L) drawn in 30% thermal probability ellipsoids showing atomic numbering schemes.



**Fig. 2.** Ortep diagram of Cu(II) complex (1) drawn in 30% thermal probability ellipsoids showing atomic numbering schemes. Selected bond lengths [Å] and bond angles [°]: Cu(1)-O(1) 1.9470(18), Cu(1)-O(2) 1.9729(17), Cu(1)-N(4) 2.0058(18), Cu(1)-O(5) 2.0110(15), O(1)-Cu(1)-O(2) 179.34(9), O(1)-Cu(1)-N(4) 87.24(8), O(2)-Cu(1)-N(4) 92.44(7), O(1)-Cu(1)-O(5) 90.64(8), O(2)-Cu(1)-O(5) 89.44(7), N(4)-Cu(1)-O(5)156.97(8), O(1)-Cu(1)-N(1) 95.84(8), O(2)-Cu(1)-N(1) 84.81(8), N(4)-Cu(1)-N(1) 109.65(8), O(5)-Cu(1)-N(1) 93.38(7), Cu(1)-O(1)-H(101)120.7(17), Cu(1)-O(1)-H(102) 118(2), H(101)-O(1)-H(102) 118(3) and N(7)-O(2)-Cu(1) 112.01(17).

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, implying that the lone pair of the benzimidazole nitrogen is only weakly involved in photo induced electron transfer (PET) to the aromatic fluorophore [26].

4-(2-Aminoethyl)benzene-1,2-diol has been utilized to evaluate the fluorescent properties of 1-(pyridin-2-ylmethyl)-2-(3-(1-(pyridin-2-ylmethyl)benzimidazol-2-yl)propyl)benzimidazole (L) and its copper(II) complex (1). Sensor (L) displayed an emission at 297 nm when excited at 277 nm in DMF and on addition of 4-(2-aminoethyl)benzene-1,2-diol the monomer fluorescence intensity decreases at 297 nm and growth of a new band at 306 nm is observed (Fig. 4) which is probably due to the formation of a host guest complex between ligand and 4-(2-aminoethyl)benzene-1,2-diol accompanied by an isoemissive point at 300 nm. The band at 306 nm is a real band with no role of solvent





**Fig. 3.** Emission spectra of (**GAB**),  $c = 6 \mu M$  at slit width 2.5, ligand (L),  $c = 6 \mu M$  at slit width 5.0 and Cu(II) complex (1) in DMF at slit width 5.0.



**Fig. 4.** Fluorescence titration of ligand (L),  $c = 6 \mu M$  with 4-(2-aminoethyl)benzene-1,2-diol in DMF with increasing 4-(2-aminoethyl)benzene-1,2-diol concentration (4.8–47.4  $\mu$ M).



Fig. 5. Fluorescence titration of ligand (L), c = 6  $\mu M$  with 1-3,4-dihydroxyphenylalanine in DMF with increasing 1-3,4-dihydroxyphenylalanine concentration (4.8–47.4  $\mu M).$ 

phenol while intensity increases on addition of 2-phenylethanamine. This suggests that our sensor (**L**) is selective to the compounds bearing both the amino and phenolic moiety, as is the case with 4-(2-aminoethyl) benzene-1,2-diol. Further sensor (**L**) is specific and selective for 4-(2-aminoethyl)benzene-1,2-diol in comparison to similar compounds like L-3,4-dihydroxyphenylalanine and 4,6-ditertiarybutylbenzene-1,2-diol (DTBC). Similarly fluorescence titration experiments of sensor (**L**) were conducted with L-3,4-dihydroxyphenylalanine and DTBC (Figs. 5 and 6), no significant change in the fluorescence emission intensity of (**L**) is observed. In conclusion results are presented as histograms at 306 nm (Fig. 7) in order to highlight the selectivity of sensor (**L**) towards 4-(2-aminoethyl)benzene-1,2-diol over L-3,4-dihydroxyphenylalanine, DTBC and 2,3-dimethyl phenol. However, intensity increases on adding 2-phenylethanamine but no new band is observed at 306 nm.

Fig. 1.9 of the Supplementary data shows the plot of  $F_0/F - F_0$  vs 1/Conc (4-(2-aminoethyl)benzene-1,2-diol) at a selected wavelength of 306 nm with (L). Straight line behavior supports the validity of the assumption of 1:1 complex formation and the association constant of (L) with 4-(2-aminoethyl)benzene-1,2-diol is calculated to be 9868  $M^{-1}$  from the slope of the line [27]. This value of association



**Fig. 6.** Fluorescence titration of ligand (L),  $c=6 \mu M$  with 4,6-ditertiarybutyl benzene1,2-diol (DTBC) in DMF with increasing DTBC concentration (4.8–47.4  $\mu$ M).



**Fig. 7.** Normalized fluorescence of sensor (L) with the addition of 8 equivalents of 4-(2-aminoethyl)benzene-1,2-diol, 4,6-tertiarybutyl benzene1,2-diol(DTBC), L-3,4-dihydroxyphenylalanine, 2,3-dimethyl phenol and 2-phenylethanamine in DMF.

constant is higher than that reported with other ligating systems. For e.g. association constant of selective sensor, coumarin aldehyde for 4-(2-aminoethyl)benzene-1,2-diol and 4-(2-amino-1-hydroxyethyl) benzene-1,2-diol is 3400 and 6500 M<sup>-1</sup> and the association constants of anthracene fluorophore bearing boronic acid and aldehyde group with 4-(2-aminoethyl)benzene-1,2-diol, 4-(1-hydroxy-2-(methylamino)ethyl)benzene-1,2-diol and catechol are 5720, 5050 and 2010 M<sup>-1</sup> [11,12]. This shows that sensor (L) exhibits strong binding affinity towards 4-(2-aminoethyl)benzene-1,2-diol.

It has been well established that nonenzymatic auto oxidation of 4-(2-aminoethyl)benzene-1,2-diol can occur in vitro into polymeric material which resembles neuromelanin. Such an autooxidation is known to be accelerated by interaction with transition-metal ions. Since copper is a trace metal and acts as a redox catalyst for the oxidation of 4-(2-aminoethyl)benzene-1,2-diol to quinones [6d], therefore titrations were performed using Cu(II) complex (1) as a catalyst with 4-(2-aminoethyl)benzene-1,2-diol in order to check the sensitivity of ligand in the complex form and also any redox activity of copper(II) metal ion with this ligand. A different pattern is observed (Fig. 8) in the fluorescence emission spectrum of copper complex; monomer

0.25 0.20 Arbitrary units 0.15 0.10 0.05 0.00 300 320 340 360 380 400 420 440 Wavelength (nm)

**Fig. 8.** Fluorescence titration of Cu (II) complex (1) ( $c=6 \mu$ M) with 4-(2-aminoethyl) benzene-1,2-diol in DMF with increasing 4-(2-aminoethyl)benzene-1,2-diol concentration (4.8–47.4  $\mu$ M).

intensity broadens and shifts to a higher wavelength on addition of 4-(2-aminoethyl)benzene-1,2-diol accompanied by the formation of a shoulder at 322 nm attributed to weak interaction of Cu(II) complex with 4-(2-aminoethyl)benzene-1,2-diol. This shows that when Cu(II) ion binds with the ligand or when ligand is used in complex form as a sensor, the sensing ability of the ligating moiety of (L) towards 4-(2-aminoethyl)benzene-1,2-diol gets weakened thereby restricting the formation of host guest complex at 306 nm. Association constant of complex (1) at 322 nm is found to be lower by 6844 M<sup>-1</sup> than the parent ligand (L) [Fig. 2.0 Supplementary data], suggesting a weaker association complex formation in comparison to the parent ligand (L).

### Conclusion

We have developed a new fluorescent sensor (L), which is found to be selective for 4-(2-aminoethyl)benzene-1,2-diol over aromatic amines and phenols. Sensor (L) is also specific and selective to 4-(2-aminoethyl)benzene-1,2-diol in comparison to other catechol amines. This has been demonstrated by conducting fluorescent titration experiments of sensor (L) with the amine (2-phenylethanamine), phenol (2,3-dimethyl phenol) catechol amine (L-3,4-dihydroxyphenylalanine) and 4,6-ditertiarybutyl benzene1,2-diol (DTBC). No significant change in the fluorescence emission intensity of (L) is observed as is the case with 4-(2-aminoethyl)benzene-1,2-diol where it responds differently, growth of a new band at 306 nm is observed due to the formation of a host guest complex between ligand and 4-(2-aminoethyl) benzene-1,2-diol accompanied by an isoemissive point at 300 nm. Association constant of (L) with 4-(2-aminoethyl)benzene-1,2-diol is found to be higher by 9868  $M^{-1}$  than the other reported ligating systems. Furthermore it is found that when a similar titration experiment was conducted with the ligand in complex form (1), the sensing ability of the ligating moiety of (L) towards 4-(2-aminoethyl)benzene-1,2-diol gets weakened thereby restricting the formation of host guest complex at 306 nm. Association constant of complex (1) is found to be lower by 6844  $M^{-1}$  than the parent ligand (L), suggesting a weaker association complex formation in comparison to the parent ligand (L).

### Acknowledgment

We gratefully acknowledge the financial support from the University of Delhi, Delhi, India for the special grant.

### **Appendix A. Supplementary material**

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC of Ligand (L) and Cu(II) complex (1) is 779380 and 779381 respectively). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2013.02.015.

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- [14] Preparation of the ligand 1-(pyridin-2-ylmethyl)-2-(3-(1-(pyridin-2-ylmethyl)) benzimidazol-2-yl)propyl)benzimidazole (L): A solution of 2-(3-(benzimidazol-2-yl)propyl)benzimidazole (GAB) (1 g,3.62mmols) in DMF was stirred for 3 h with K<sub>2</sub>CO<sub>3</sub> (1.25 g,9.05mmols) at 70 °C. When turbidity appeared, 2-(chloromethyl)pyridine (1.48 g, 9.05mmols) was added and the solution was stirred for 72 h continuously at 70 °C. Subsequently the solvent was stripped off on a rotatory evaporator and the residue was treated with small amount of distilled water to obtain a brown colored crude product. The product was recrystallised from hot acetonitrile and water (2:1) and a light brownish crystalline powder was obtained. Yield: 55%. <sup>1</sup>H NMR:δ<sub>H</sub> (400 MHz, d<sub>6</sub> DMSO, Me<sub>4</sub>Si): 2.98-3.04(4H, t, CH<sub>2</sub>), 2.24-2.33 (2H, q, CH<sub>2</sub>), 5.55 (4H, s, NCH<sub>2</sub>), 7.07-7.13 (2H, m, benz), 7.16-7.20 (2H, m, pyr), 7.37-7.41(2H, m, benz), 7.50-7.54 (2H, m, pyr), 7.61-7.65 (2H, m, pyr), 8.37-8.40 (2H, d, pyr); <sup>13</sup>C NMR: (400 MHz; d<sub>6</sub> DMSO):156.5, 149,142.5,137.6,136,123.8,121, 122.119,49,28, 26; Anal Calcd for C<sub>31</sub> H<sub>33</sub> N<sub>7</sub> O<sub>2</sub>: C 69.5, H 6.1, N 18.3, Found: C 69.2, H 6.2, N18.1; UV data: λ<sub>max</sub>/cm<sup>-1</sup> 3366 (OH), 1463 (C=N-C=C) and 1616 (C=N).
- [15] Preparation of Cu(II) complex (1): A methanolic solution (5 ml) of Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O (52.7 mg, 0.22 mmol) was added to a methanolic solution (15 ml) of the ligand (100 mg, 0.22 mmol). The resulting green colored solution was stirred for 30 min's. A light green colored product was formed which was centrifuged, washed with small amounts of cold methanol and dried over P<sub>2</sub>O<sub>5</sub>. Yield: 45%. Anal Calcd for C<sub>30</sub> H<sub>32</sub> Cu N<sub>8</sub> O<sub>8</sub>:C 51.7, H 4.6, N16.1, Found: C 52.0, H 4.4, N16.3; U.V Visible data: λ<sub>max</sub>(DMF)/nm [logc/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>]=268 [4.16], 277 [4.12], 284 [4.06], 800 [1.75]; v<sub>max</sub>/cm<sup>-1</sup> 3432 (OH), 1456 (C=N-C=C), 1594 (C=N), 1011, 1336 (O-N-O (symm)) and1435 (O-N-O (asym))
- [16] X-ray diffraction data were collected on an Oxford Diffraction Xcalibur CCD diffractometer with graphite monochromated (Mo–K<sub> $\alpha$ </sub> radiation,  $\lambda = 0.71073$  Ű), temperature of 298(2) K at IIT Bombay. The data were corrected for Lorentz and polarization effects. Multi-scan absorption correction was applied. The data reduction was performed using the CrysAlis software package [28]. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares method on F<sup>2</sup> (SHELXL-97) [29]. All calculations were carried out using the Wings package of the crystallographic programs [30]. For the molecular graphics, the programs ORTEP-3 [31] and Mercury were used [32]. Crystal data of [ligand (L):C<sub>31</sub>H<sub>31</sub>Ny O<sub>2</sub>, M<sub>r</sub>=533.63, T=150(2) K, λ=0.71073 Å, Monoclinic, P 21/n, a=10.7497(6) Å α=90 °,b=19.0156(9) Å, β=104.576(6) °, c= 13.8566(7) Å,  $\gamma = 90^{\circ}$ , V = 2741.3(2) Å<sup>3</sup>, Z = 4, d = 1.286 mg/m<sup>3</sup>, Absorption coefficient 0.084 mm<sup>-1</sup>, F(000) = 1116, 0.23 × 0.16 × 0.13 mm, Limiting indices [I>2sigma(I)]: R1=0.0581, wR<sub>2</sub>=0.1522, R indices (all data): R1=0.1263,  $wR_2 = 0.1709$ . Crystal data of Cu(II) complex (1):C<sub>30</sub> H<sub>32</sub> Cu N<sub>8</sub> O<sub>8</sub>, M<sub>r</sub> = 696.18, T=150(2) K,  $\lambda$ =0.71073 A, Monoclinic, P 21/n, a=9.8146(4) Å,  $\alpha$ =90°, b=19.2684(9) Å, β=99.705(4)°, c=15.8600(7) Å, γ=90°, V=2956.4(2) Å<sup>3</sup>,  $Z=4, \ d=1.564 \ mg/m^3 \ Absorption \ coefficient=0.807 \ mm^{-1}, \ F(000)=1444, \\ 0.38 \times 0.33 \times 0.31 \ mm, \ Limiting \ indices \ -11<=h<=11, \ -22<=k<=22,$  $-18 \le 1 \le 18$ , Reflections collected/unique 21455/5193 [R(int) = 0.0559],

 $2\theta\!=\!25.00,$  GOF=0.810, Final R indices [I>2sigma(I)]: R1=0.0330, wR\_2\!=\!0.0568, R indices (all data): R1=0.0608, wR\_2=0.0594.

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$$F_0/F - F_0 = \left[ \Phi_m \ \epsilon_m / \left( \Phi_p \epsilon_{p-} \Phi_m \ \epsilon_m \right) \right] * (1/K_a C_d + 1)$$

where  $F_0$  and F denote the measured fluorescence intensity prior to and after adding 4-(2-aminoethyl)benzene-1,2-diol.  $\Phi_M$  and  $\Phi_p$  are fluorescence quantum yields of the monomer and complex, respectively. The fluorescence titration spectra as well as the plot of  $F_0/(F-F_0)$  versus  $1/C_d$  are depicted in [Fig. 1.9, Fig. 2.0 Supplementary data], in which the linear behavior of the plot reconfirms the 1:1 complex formation. Using slope and intercept K<sub>a</sub> value is calculated.

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