Electronic Supplementary Information

Dimeric copper(II) Complex of a New Schiff Base Ligand: Effect of Morphology on the Catalytic Oxidation of Aromatic Alcohol

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Contents:

EXPERIMENTAL SECTION

Materials and Method

o-Phenylenediamine (Thomas Baker, Mumbai), β-Alanine(Merck), 2-Hydroxy-1-Naphaldehyde (Alfa-Aesar), K_2CO_3(Thomas Baker), $Cu(NO_3)_2$(Thomas Baker), the alcohol(Merck) and 70% TBHP(Lancaster) were used as obtained. 2-aminoethylbenzimidazole dihydrochloride (AB.2HCl) was prepared according to the procedure as reported by Cescon and Day.

Instrumentations

Elemental analysis of the ligand and their complexes were obtained on VARIO EL III from USIC, University of Delhi, India. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400MHz JEOL ECX-400P spectrometer in d_6-DMSO. IR spectra were recorded on a Perkin-Elmer FT-IR-2000 spectrometer using KBr discs in the range of 400-4000cm^{-1}. UV-Vis spectra were recorded in DMF with a Shimadzu UV-Vis-1601 spectrometer. The morphological changes in the copper(II) complexes was studied by scanning electron microscopy (SEM) model FEI Quanta 200F with oxford –EDS system IE 250 X Max 80 with gold coating in SMITA research lab IIT Delhi, India. GC-MS spectra were recorded at AIRF, JNU, New Delhi on a GCMS-QP2010 (plus) Schimadzu instrument. The powder X-ray diffraction patterns were recorded using High resolution D8 Discover Bruker diffractometer, equipped with point detector (scintillation counter), employing monochromatized Cu $K_{\alpha 1}$ radiation with a scan rate of 1.0 second/step and step size 0.02° at 298 K over the range of $2\theta = 5°$ to 35°. The Photoluminescence spectral measurements of the sample were carried out using Horiba Jobin Yvon Fluorolog modular spectrofluorimeter at room temperature employing a continuous-wave xenon lamp source.

X-ray crystallography

Single crystals of Schiff base ligand **HL** and complex suitable for X-ray diffraction studies were grown by slow evaporation in methanol**.** The intensity data for were collected at 298(2) K on an X’calibur CCD diffractometer with graphite monochromatized Mo/Kα. Radiation (λ=0.71073 Å) from USIC, University of Delhi, Delhi, India. For H**L**, a total of 11227 reflections were measured of which 3328 were unique and 2198 were considered observed ($I > 2\sigma$ (I)]. For complex a total of 8745 reflections were measured of which 3055 were unique and 2313 were considered observed ($I > 2\sigma(I)$]. The data were corrected for Lorentz and polarization effects. Multi-scan absorption correction was applied. The structure was solved by direct methods using SHELXS-97[1] and refined by full-matrix least-squares refinement techniques on F^2, using SHELXL-97.[1] All calculations were done with the help of WINGX programme[2] For the molecular graphics, the programme Diamond2[3] and Mercury[4] were used. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with U_{iso} values of 1.2 times the U_{iso} values of their respective carrier atoms. The final residual index for H**L** are; *R* 0.0651, *R*w 0.1204 for the observed and *R* 0.1063, *R*w 0.1354 for all reflections using 226 parameters and zero restraint. The final residual index for complex is; *R* 0.0471, *R*w 0.1208 for the observed and *R* 0.0687, *R*w 0.1439 for all reflections using 257 parameters and one restraints. Details of the crystallographic data and structure refinement for ligand **HL** and complex are given in Table 1.

Synthesis of Schiff base Ligand (HL)

2-aminoethyl benzimidazolyl dihydrochloride (AB.2HCl) was prepared as reported earlier.[5] This was dissolved in water and neutralized by adding requisite amount of aqueous K_2CO_3. A stirred methanolic solution of 2-hydroxy-1-naphthaldehyde was added slowly to the above solution. After about ½ hr a yellow solid separated out. The solid was filtered off, washed with water and petroleum ether, dried in vacuo over P_2O_5. It was finally recrystallized from acetonitrile.

Anal. Found(Calc.) for $C_{20}H_{19}N_3O_2$: C 72.5(72.1), H 5.8(5.7), N 12.7(12.6); Selected IR(KBr, cm^{-1}): $\nu_{(-C=N-C=C-)}$ 1362, $\nu_{(NH)(H\text{-bonded})}$ 2919, $\nu_{(C=N)}$ 1635; ^1H NMR (400 MHz, DMSO-d_6, δppm): 13.9(s,1H,OH), 12.2(s,1H,NH), 9.1(s,1H,-CH=N-), 7.9(d,1H,aromatic),6.6-7.6(d,m,7H,aromatic), 4.1(t,-CH_2-), 3.2(t,-CH_2-); UV-Vis λ_{max}/nm(log ε) in DMF: 422(3.7), 306(3.8), 283(3.7), 272(3.9).

The Ligand was dissolved in MeCN : MeOH (3:2) and left for slow evaporation, after a few days transparent light yellow colored crystal separated out. A suitable crystal was used for single crystal X-ray studies.

Synthesis of Complex $[Cu(L)NO_3]_2$:

To a solution of ligand (100mg, 0.3 mmol) in 20 ml methanol, $Cu(NO_3)_2$ (51 mg, 0.3 mmol) dissolved in 5 ml of methanol was added drop wise with constant stirring. The resulting mixture was refluxed at 80 °C for 1 hour. Thereafter the green colored solution so obtained was transferred to a 100 ml beaker and allowed to stand at room temperature. The green colored crystal obtained were filtered air dried and analyzed for the composition. Anal. Found(Calc.) for $C_{40}H_{32}N_8O_8Cu_2$: C 54.1(54.5), H 3.8(3.6), N 12.6(12.7); Selected IR(KBr, cm^{-1}); $\nu_{(-C=N-C=C-)}$ 1458, $\nu_{(NH)(H\text{-bonded})}$ 3067, $\nu_{(C=N)}$ 1625, $\nu_{C=C}$ benzene 747; UV-Vis λ_{max}/nm(log ε) in DMF: 272(4.1), 302(3.9), 314(3.9), 386(3.6), 627(2.1).

Spectroscopic investigations

The electronic spectra of the ligand and complexes are present in experimental section. The UV spectra of the ligand show three absorption maxima in the range of 270-320nm. The band at 272 nm and 283 nm correspond to **π-π*** transition characterizing the benzimidazole group. The band at 314 nm is assign to the **n-π*** transition. In complex the band due to **π-π*** transition is shifted to higher wavelength while the **n- π*** transition merges with an additional broad band due to the ligand to metal charge transfer (LMCT) from the napthanol oxygen to an empty d orbital of metal ion. Due to d^9 configuration of copper(II) a broad but a much less intense d-d band is observed in the region of 610-630 nm.

The IR spectra of the ligand have characteristic IR band at 1635 cm^{-1} due to ν (C=N) azomethine. The band between 1350 cm^{-1} and 741 cm^{-1} is assigned to ν(C=N-C=N) stretching of the benzimidazole group. On complexation these band moves towards the lower wave number by 20-30 cm^{-1} indicating a coordination of azomethine nitrogen and imine nitrogen to the copper. The characteristic stretching frequeries for the coordination anion is also observed.

^{1}H NMR and ^{13}C NMR:

The ^{1}HNMR spectral of the ligand in d_6-DMSO shows a broad signal at 13.9 ppm and 12.3 ppm due to the 2-naphthanol OH and benzimidazole NH respectively. The signal at 9.1 correspond to the (-CH=N-) azomethine proton. The signal due to aromatic proton is lies in between 6.6 to 7.9 ppm. The two triplets due to aliphatic CH_2 proton are observed at 3.2 ppm and 4.1 ppm as shown in Figure S1.

^{13}CNMR in d$_6$-DMSO shows signal at 48.7 ppm and 29.9 ppm assigned for two aliphatic carbons. The signal between 118.4 ppm to 128.8 ppm corresponding to the aromatic carbon of both ring. The aromatic carbon attached to the naphthanol oxygen (177.16ppm), azomethine nitrogen (159.27ppm) and ring nitrogen (152.17ppm) comes at larger $\Delta\delta$ value as shown in Figure S2.

Catalytic Activity studies:

Copper(II) complex was used heterogeneously for the oxidation of p-chloro benzyl alcohol to its respective aldehyde. In a typical reaction, catalyst (0.011 mmol), benzyl alcohol (0.11 mmol), and Oxidant (0.056 mmol, 70%) in ratio of catalyst: substrate: oxidant (1:10:5) were mixed in 15 mL dichloromethane and heated at 35-40°C for a 4 hrs. The progress of the reaction was monitored by TLC and formation of DNP derivative confirms the formation of p-chlorobenzaldehyde which was the only product observed in all the cases. The reaction mixture was centrifuged after a 4 hr reaction to isolate the copper(II) catalyst. The clear filtrate of the reaction mixture was checked for any dissolution of the catalyst during reaction, no band in the visible range of 500-900nm was observed ruling out the possibility of any dissolution of the copper(II) catalyst. The clear filtrate was subjected to GC-MS analysis and the formation of p-chlorobenzaldehyde was confirmed. The complex was reused for p-chlorobenzyl alcohol oxidation and a decrease in the yield of benzaldehyde is observed for repeat cycles, as analyzed through GC-MS using naphthalene as an internal standard.

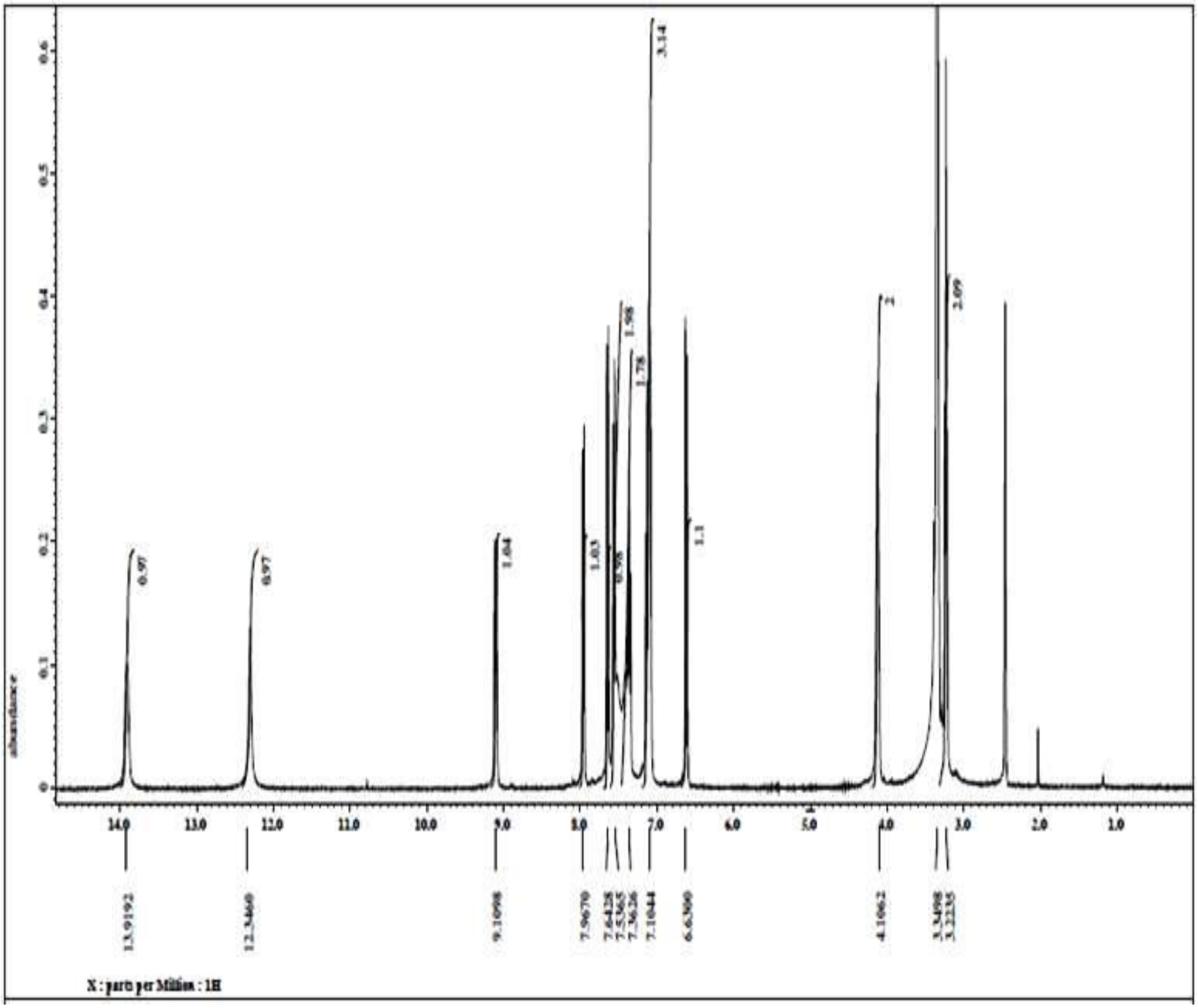

Figure S1. ^{1}H-NMR Spectra of the Ligand in d^{6}-DMSO.

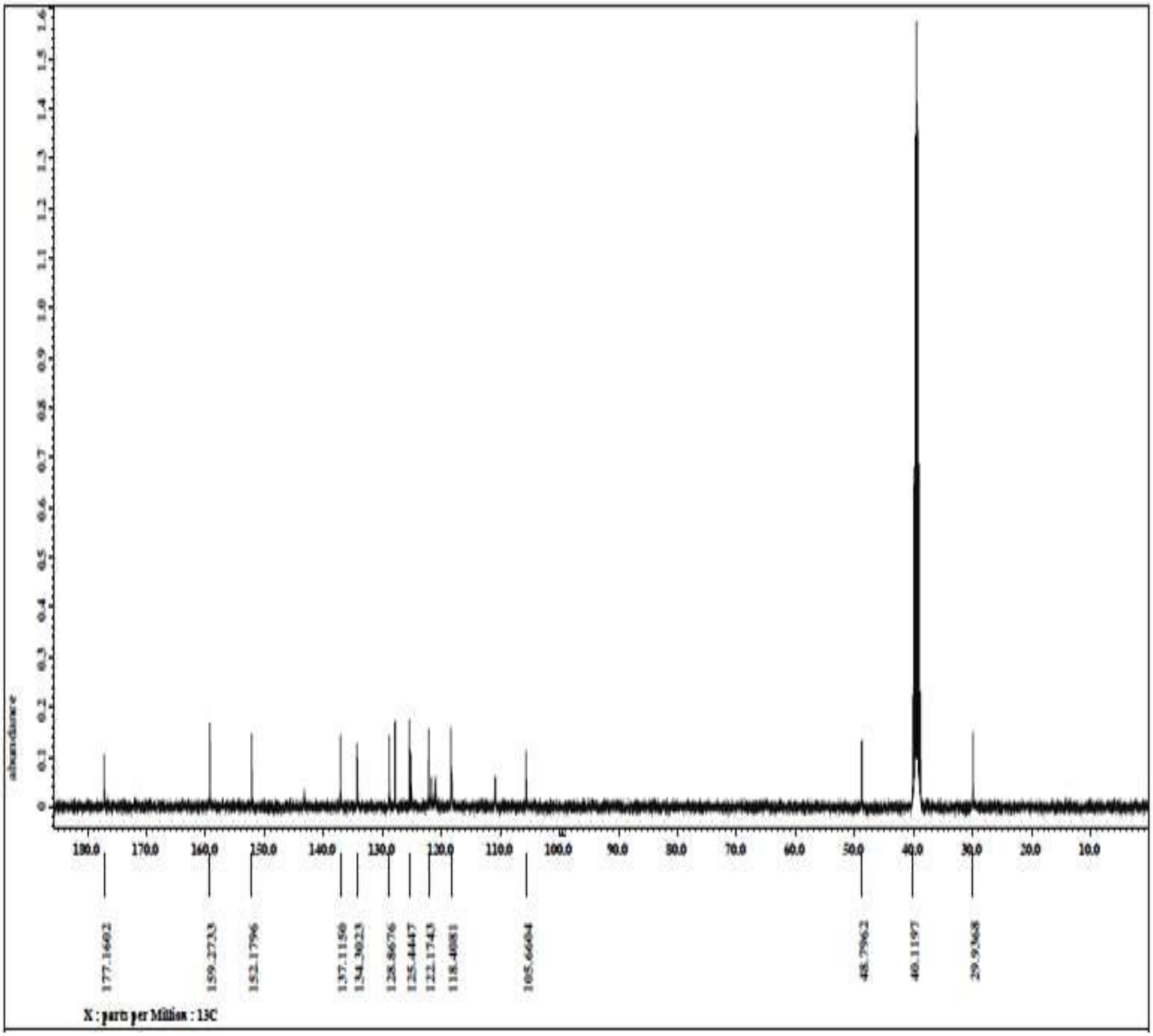

Figure S2. ^{13}C-NMR Spectra of the Ligand in d^{6}-DMSO.

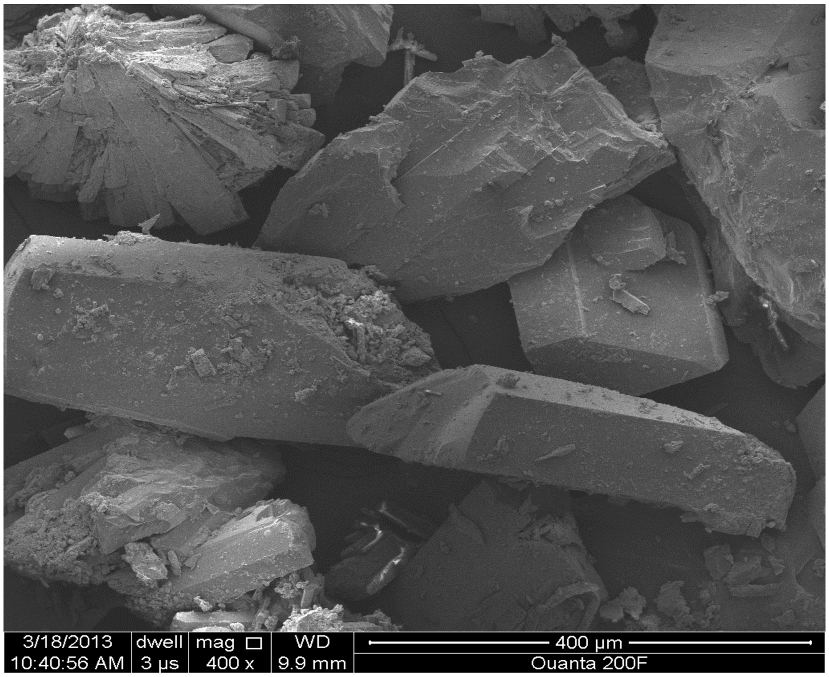

Figure S3. The morphology of the dimeric complex with oxidant.

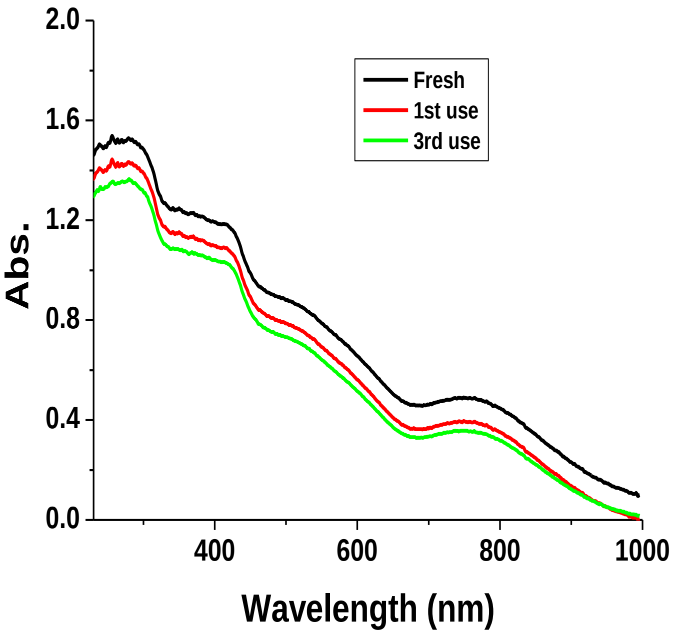

Figure S4. UV-Visible spectra of the complex in solid state in different run.

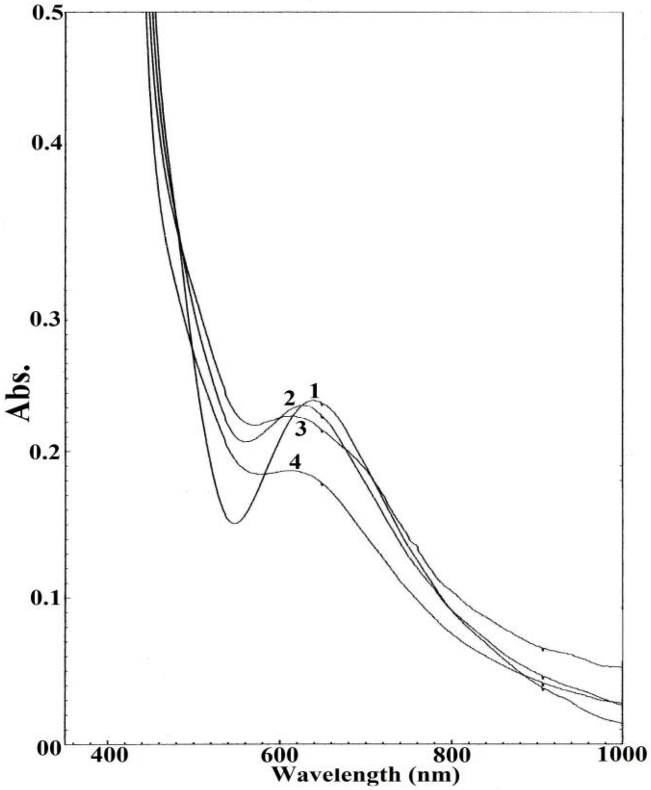

Figure S5. Variation in the d-d band of the complex in solution of equal concentration (1) Without use (2) 1st use (3) 2nd use (4) 3rd use.

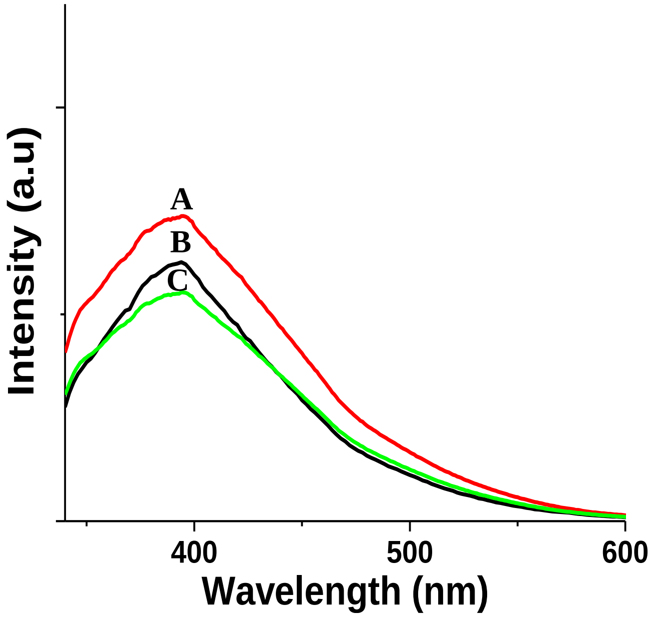

Figure S6. Photoluminescence spectra of complex in solid form in different run. (A) without use (B) 1st use (C) 3rd use.

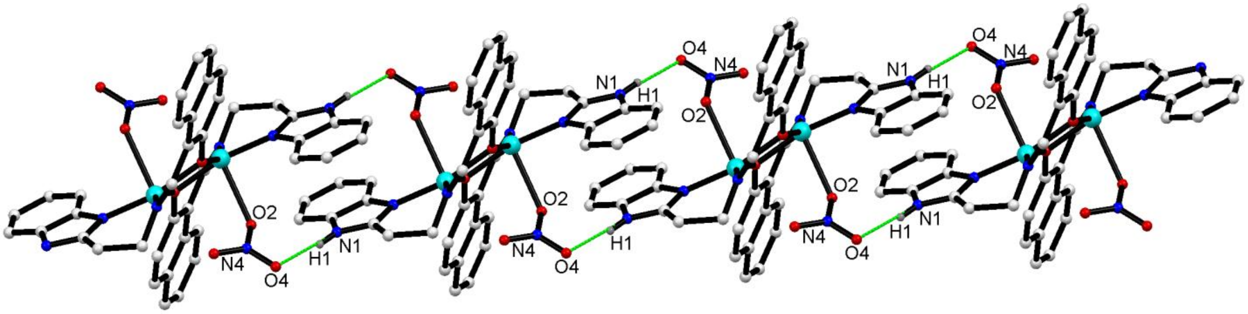

Figure S7. Intermolecular H-bonding N1-H1…..O4 {2.112(4) Å}, Cu2….O2 {2.005(3) Å}, N1-H1….O4 {172.69(13)°}. (i) –x+1, -y+1, -z+2.

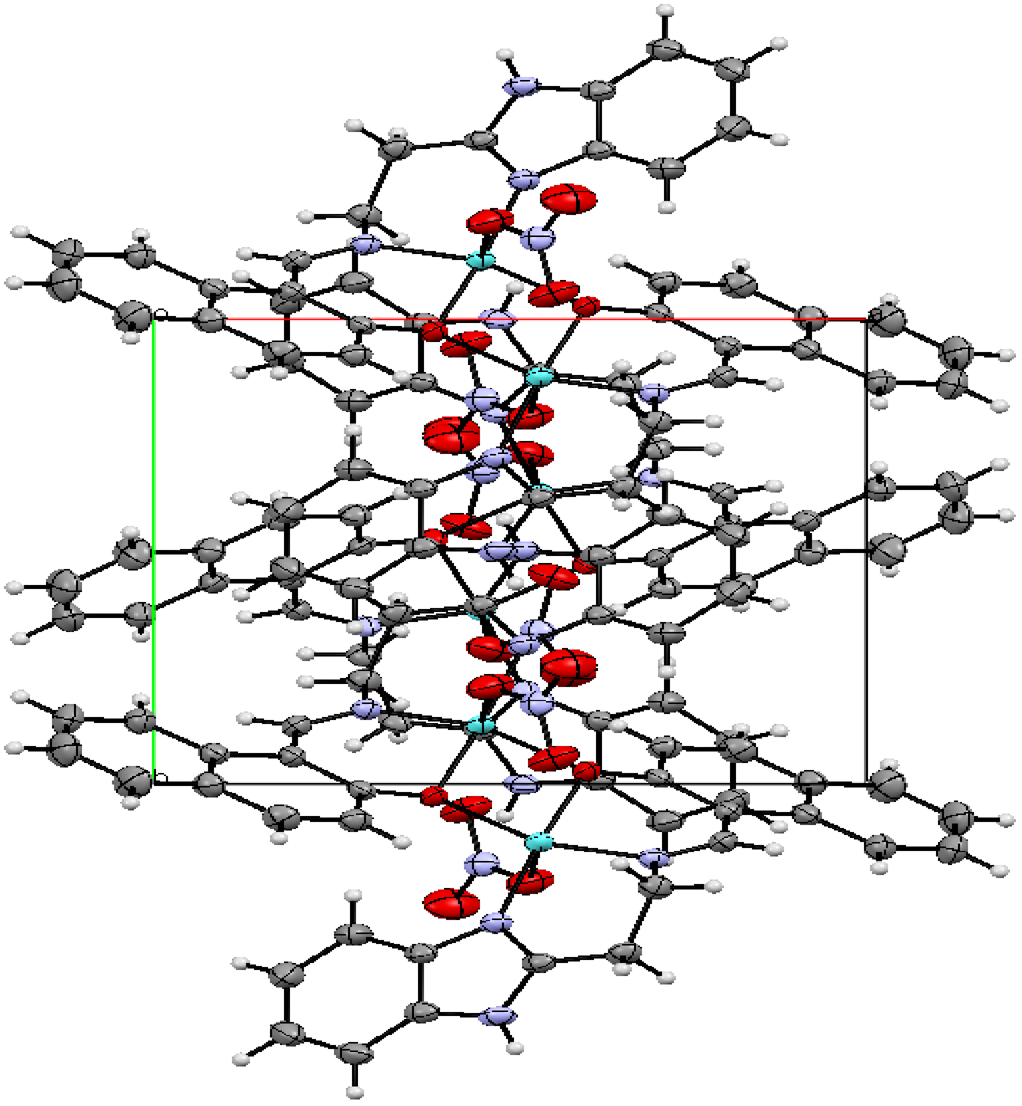

Figure S8. Unit cell packing arrangement of Dimeric complex along the C-axis

Tables

Table S1. Crystallographic Data and Structure Refinement of Ligand (HL) and its complex

	Ligand	**Complex**
Empirical formula	**$C_{20}H_{19}N_3O_2$**	**$C_{40}H_{32}Cu_2N_8O_2$**
M	333.38	879.82
Temp.(K)	291(2)	291(2)
Wavelength/ Å	0.71073	0.71073
Crystal system P-1	Monoclinic	Monoclinic
Space group	P 21/n	P 21/n
a/ Å	16.5776(19)	11.1837(7)
b/ Å	4.8180(5)	10.1047(6)
c/ Å	21.372(3)	15.9112(10)
Volume	1706.2(3) Å^3	1790.67(19)
Z	4	2
D_c/ Mg/m^3	1.298	1.632
μ/mm^{-1}	0.086	1.257
F(000)	704	900
R(int)	0.0426	0.0408
Crystal size/mm^3	0.12 x 0.10 x 0.08	0.18×0.13×0.12
Reflections collected	11227	14366
Independent reflections	3328	3516
Goodness-of-fit on F^2	1.072	1.097
R1, wR2	0.0651, 0.1204	0.0335, 0.0859
R indices (all data)	0.1063, 0.1354	0.0372, 0.0859
Largest diff. peak and hole/ e.Å^{-3}	0.186 and -0.207	0.491 and -0.389

Table S2. Selected Bond lengths [Å] and angles [°] for complex.

Complex	
N(2)-Cu(1)	1.9646(17)
N(3)-Cu(1)	1.9473(17)
O(1)-Cu(1)	1.9510(14)
O(1)-Cu(1)#1	1.9689(13)
Cu(1)-O(1)#1	1.9689(13)
Cu(1)-Cu(1)#1	3.0029(5)
N(3)-Cu(1)-O(1)	88.21(6)
N(3)-Cu(1)-N(2)	92.81(7)
O(1)-Cu(1)-N(2)	168.13(7)
N(3)-Cu(1)-O(1)#1	158.17(7)
O(1)-Cu(1)-O(1)#1	80.00(6)
N(2)-Cu(1)-O(1)#1	102.51(7)
N(3)-Cu(1)-Cu(1)#1	126.04(5)
O(1)-Cu(1)-Cu(1)#1	40.22(4)
N(2)-Cu(1)-Cu(1)#1	141.06(5)
O(1)#1-Cu(1)-Cu(1)#1	39.78(4)

Table S3. Comparison of percentage conversion after reusing the copper(II) complex.

S.No.	Catalyst	Reusability	Yield* (%)
1	**$[Cu_2(L)_2](NO_3)_2$**	1st use	84
		2nd use	74
		3rd use	66

References

1. Oxford Diffraction CrysAlis Software System, Ver. 1.171.32.
   (Oxford Diffraction Ltd. Abingdon, UK) 2007.
2. G. M. Sheldrick, Acta Crystallogr, 2008, **64** A, 112.
3. L. J. Farrugia, J. Appl. Crstallogr, 1999, **32**, 837.
4. A. L. Spek, J. Appl. Crstallogr, 2003, **36**, 7.
5. L. A. Cescon, A. R .Day, *J. Org. Chem*, 1962, **27**, 581.