Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information (ESI)

Exploring catalytic and bio-catalytic activities of structurally characterised Cu(II) and Mn(III) complexes: histidine recognition and photo-catalytic application of Cu(II) complex and derived CuOnano-cubes

Babli Kumari[a], Samapti Kundu[b], Kajari Ghosh[a], Mahuya Banerjee,[a] Swapan Kumar Pradhan[b], Sk. Manirul Islam,[c*] Paula Brandão[d], Vítor Félix[d*] and Debasis Das[a*]

a) Department of Chemistry, The University of Burdwan, Burdwan, 713104, W.B., India
b) Departmentof Physics, The University of Burdwan, Burdwan, 713104, W.B., India
c) Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, India
d) Department of Chemistry, CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193, Aveiro, Portugal

1. General method for fluorescence titration

The stock solution of complex 3 and histidine are prepared in ethanol/water (1/1, v/v). Working solutions are prepared from their respective stock solutions by proper dilution. Path length of the cell used for emission study is 1cm.

2. Job's plot from fluorescence experiments

A series of solutions containing complex 3 and histidineare prepared in ethanol/ water (1/1, v/v) such that the total concentration of [complex3 + histidine] remain constant (50 μM) in all the sets. The mole fractionof 3 is varied from 0.1 to 0.9. The fluorescence intensities are plotted against the mole fraction of complex 3 to get the stoichiometry of [complex 3 –histidine] adduct.

3. Determination of quantum yield

Fluorescence quantum yields (Φ) are estimated by integratingthe area under the fluorescence curves using the equation,

$$\varphi_{sample} = \varphi_{ref} \times [A_{sample}/A_{ref}] \times [OD_{ref}/OD_{sample}]$$

where A is the area under the fluorescence spectra and OD is optical density of the compound at the excitation wavelength. Tryptophan is used as reference with a known Φ_{ref} value of 0.14 in water. [1] The area of the emission spectrum is integrated using the software available in the instrument. Φ_{sample} and Φ_{ref} are the fluorescence quantum yields of the sample and reference respectively. A_{sample} and A_{ref} are the area under the fluorescence spectra of the sample and the reference, respectively. OD_{sample} and OD_{ref} are the corresponding optical densities of the sample and the reference solution at the wavelength of excitation. η_{sample} and η_{ref} are the refractive indeces of the sample and reference, respectively.

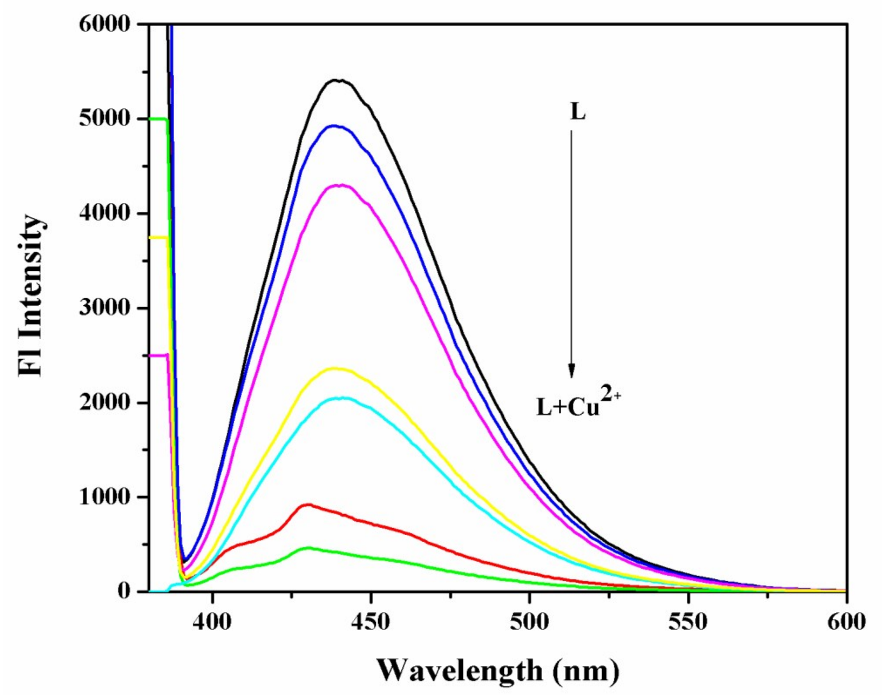

Fig. S1 Changes in fluorescence spectra of L in HEPES buffer (0.1 M, ethanol/water, 1/1, v/v, pH 7.4) upon gradual addition of Cu^{2+}(λ_{ex} = 380nm; λ_{em} = 440nm).

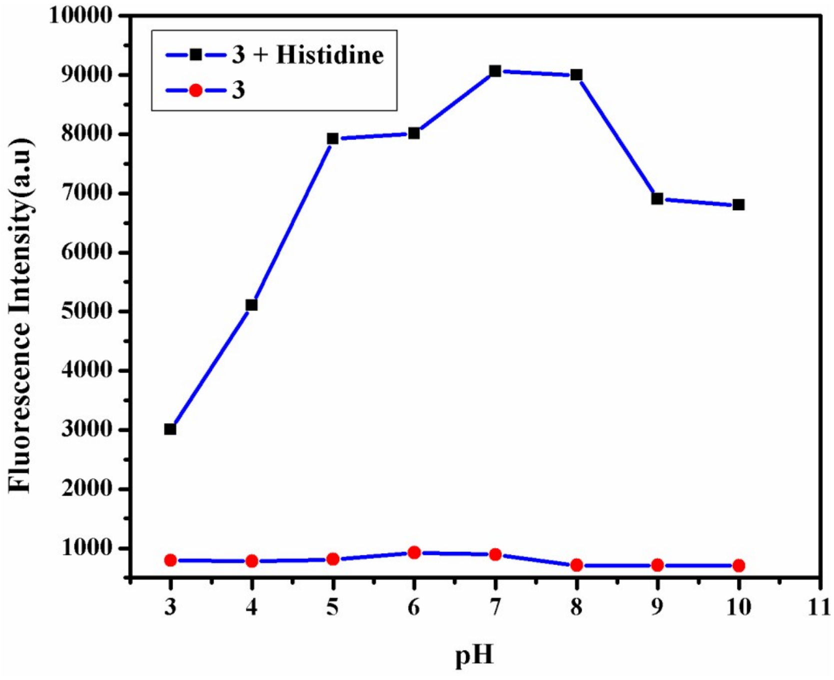

Fig. S2 Effect of pH on emission intensities of 3 in absence and presence of Histidine

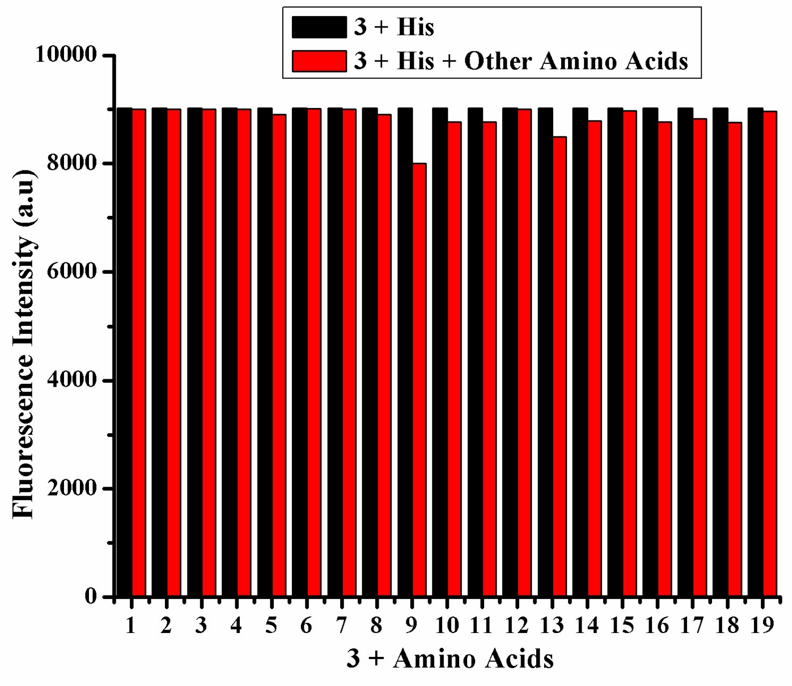

Fig.S3 Emission intensities of (complex 3 + histidine) in presence of different amino acids.

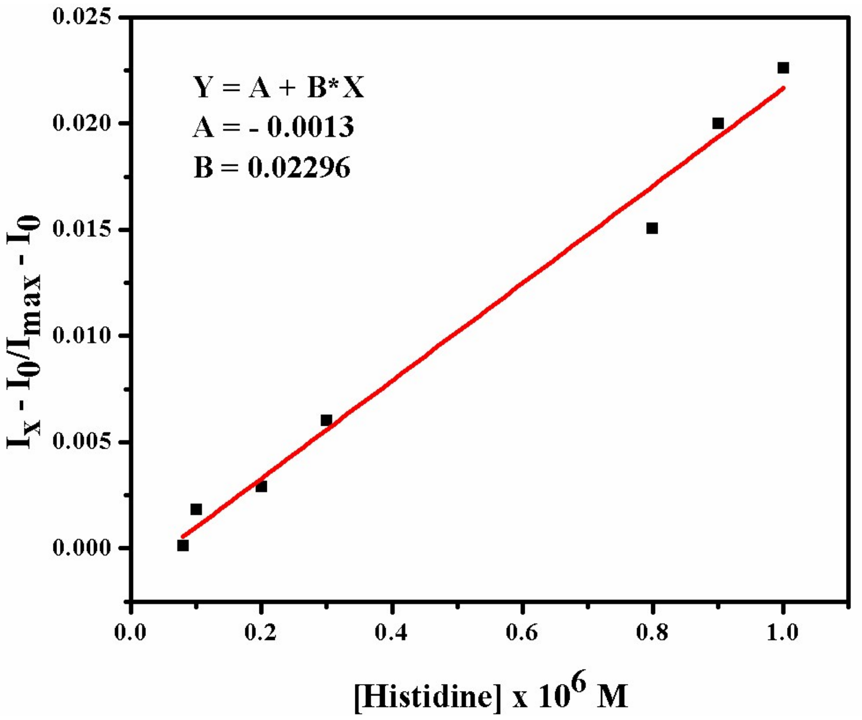

Fig. S4 Emission intensity of complex 3 as a function of added histidine in ethanol-water (1/1, v/v); $\lambda_{ex.}$ = 380 nm; λ_{em} = 440nm.

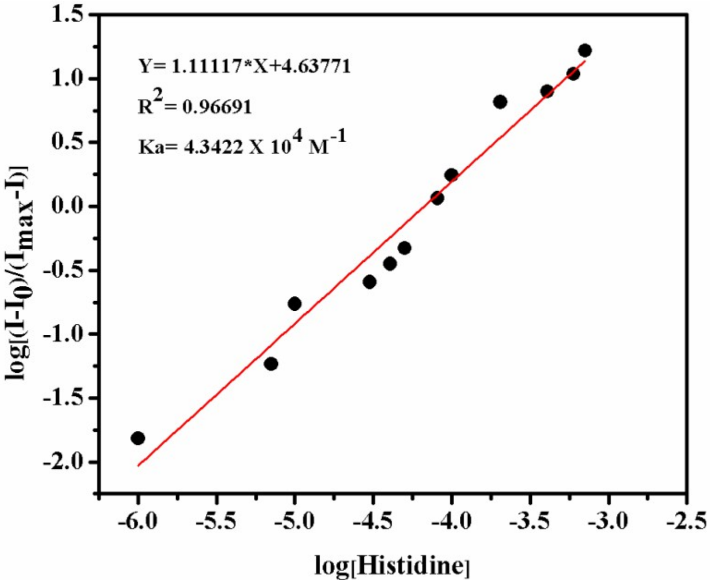

Fig. S5 Hill plot for determination of binding constant of complex 3 for histidine in said solvent.

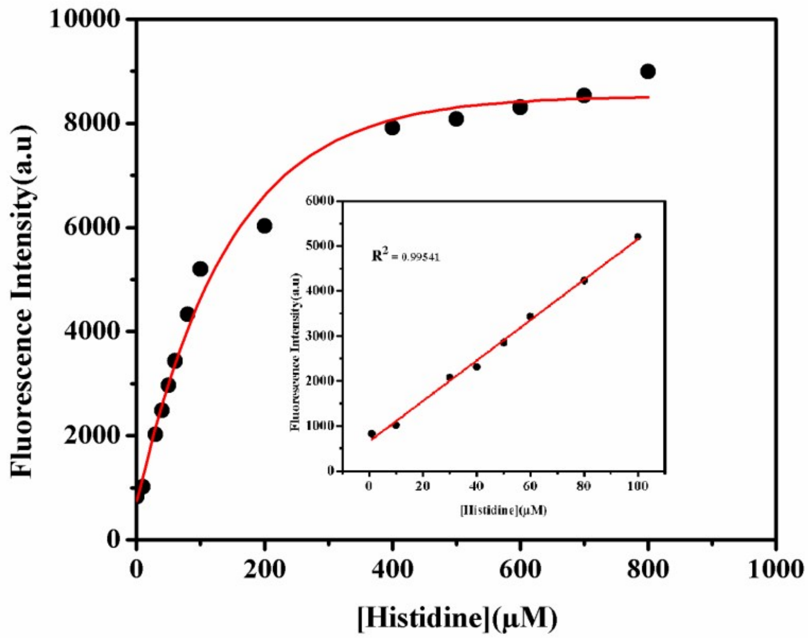

Fig. S6 Plot of emission intensity of complex 3 as a function of added histidine in said solvent, λ_{ex} = 380 nm; λ_{em} = 440 nm.

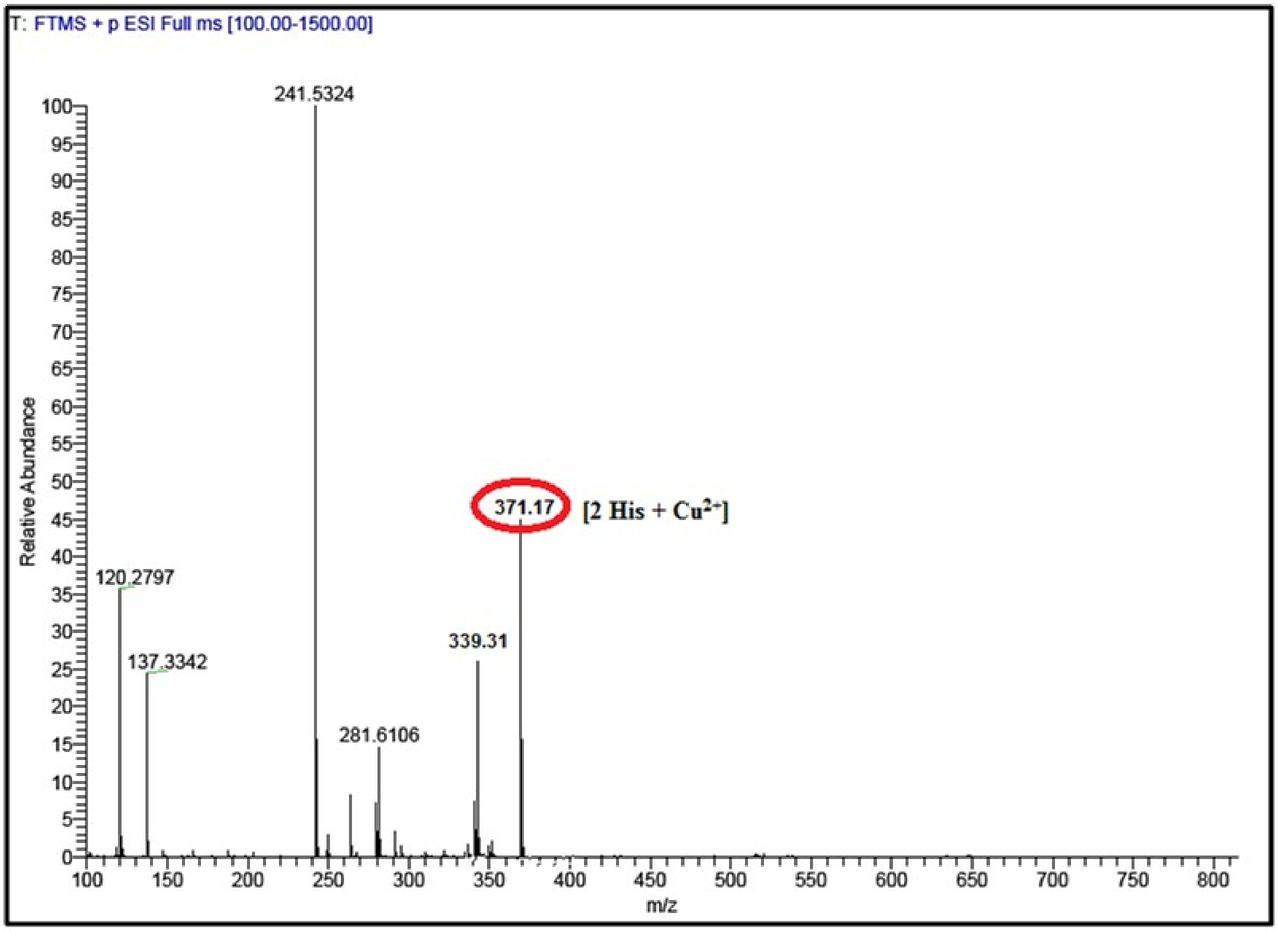

Fig. S7 ESI-MS spectrum of [complex 3- His] adduct

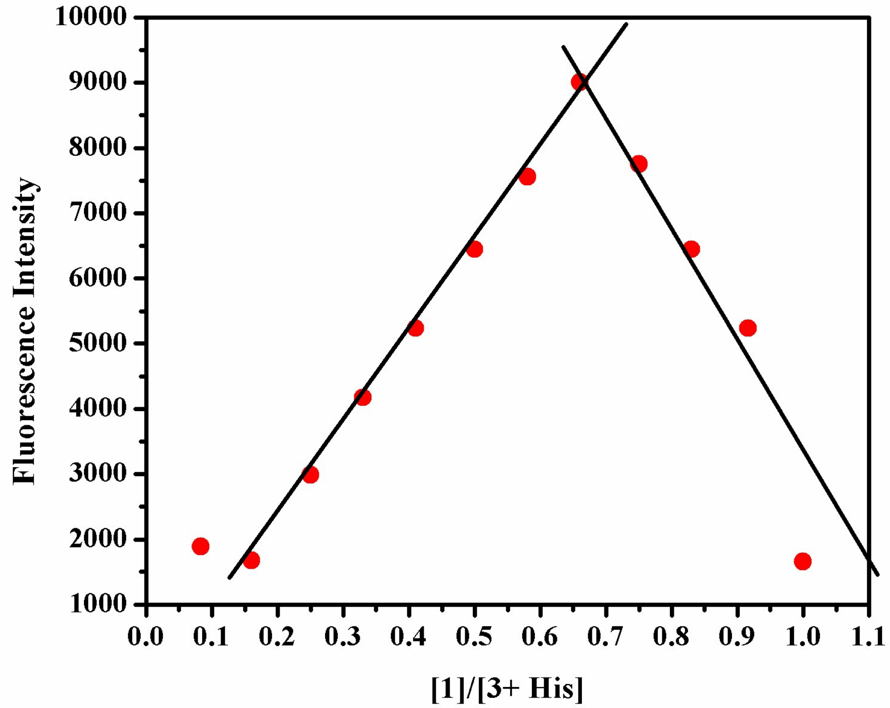

Fig. S8 Job's plot for determination of stoichiometry of the adduct between complex 3 and histidine.

Catecholaselike activity

Catecholase like activities of **3** and **4** have been performed using 3, 5-di-tertiarybutyl catechol (DTBC) for its low redox potential and easy monitoring of absorbance ~400 nm (corresponding o-quinone, DTBQ). The solutions of **3** and **4** are treated with different concentration of DTBC (10 to 100 equiv.) to determine the effect of its concentration on reaction rate and evaluate different kinetic parameters (Table S1, ESI). The rate constants are calculated from log[Aα/(Aα - At)] vs. time plot. At low DTBC concentration, first order kinetics is observed. However, with increasing DTBC concentration, saturation is observed for both **3** (Fig.S9, ESI) and **4** (Fig.S10, ESI). The activities of **3** and **4** are monitored at 396 nm and 400 nm respectively (Fig. S11 and

S12, ESI).The rate constants are plotted against DTBC concentration using Michaelis–Menten approach of enzymatic kinetics to obtain the Lineweaver-Burk(double reciprocal) plot. The rate constant (turn over number, Kcat), maximum velocity (Vmax) and binding constant (KM) are calculated from the plot: 1/V vs. 1/[S] (Fig S13 and Fig S14, ESI and Table 2), using the equation 1/V = {KM/Vmax} X {1/[S]} + 1/Vmax. The probable mechanism for the 3,5-DTBC oxidation catalyzed by the complexes proposed on the basis of the structures obtained from the ESI-MS study of the complexes after addition of 3,5-DTBC [1,2] (Fig S15 and Fig S16, ESI).

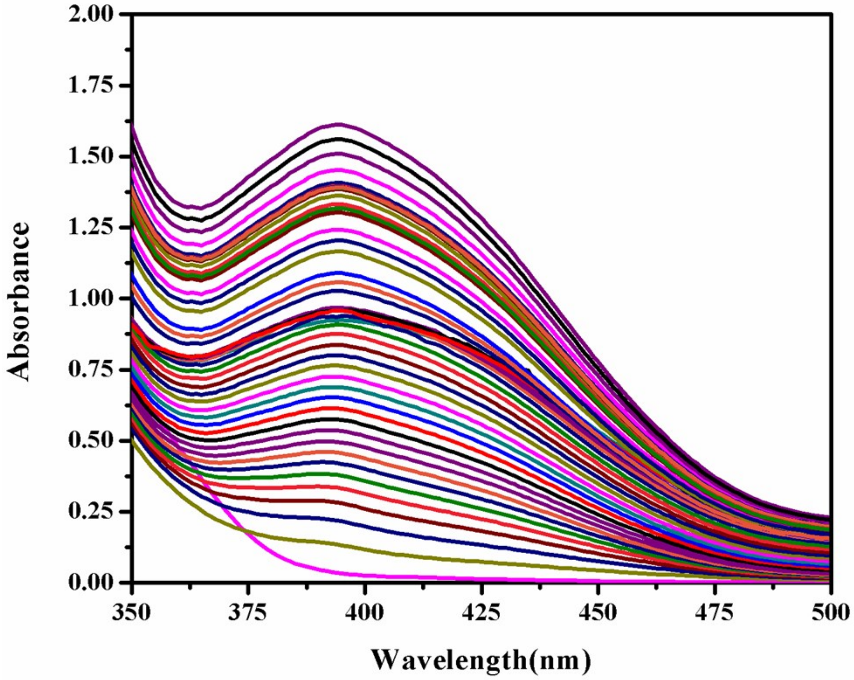

Fig. S9 Increase of absorbance of quinone band at 396nm after addition of 3, 5-di-tertiary butyl catechol (100 fold, 1× 10^{-2}M) to 3 (1× 10^{-4}M) in methanol at 5 min interval.

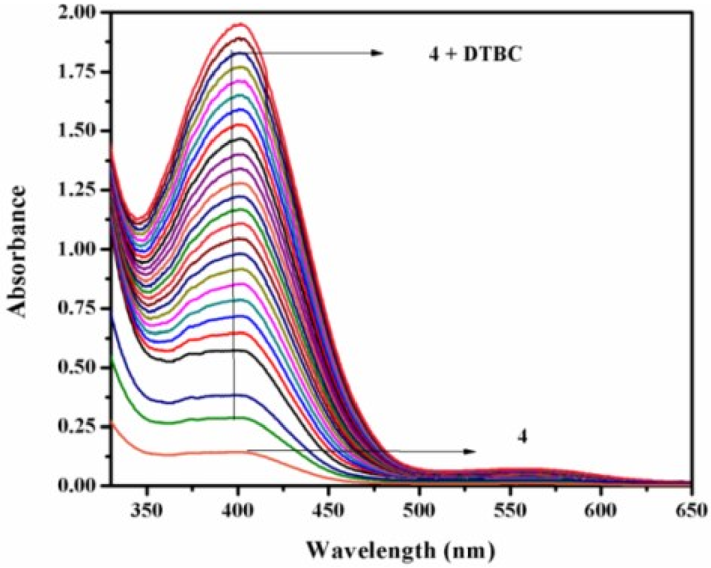

Figure **10** Increase of absorbance at 400 nm (quinone band) upon addition of [DTBC] (1× 10^{-2}M) to **4** (1× 10^{-4}M) in methanol (time interval,5 min).

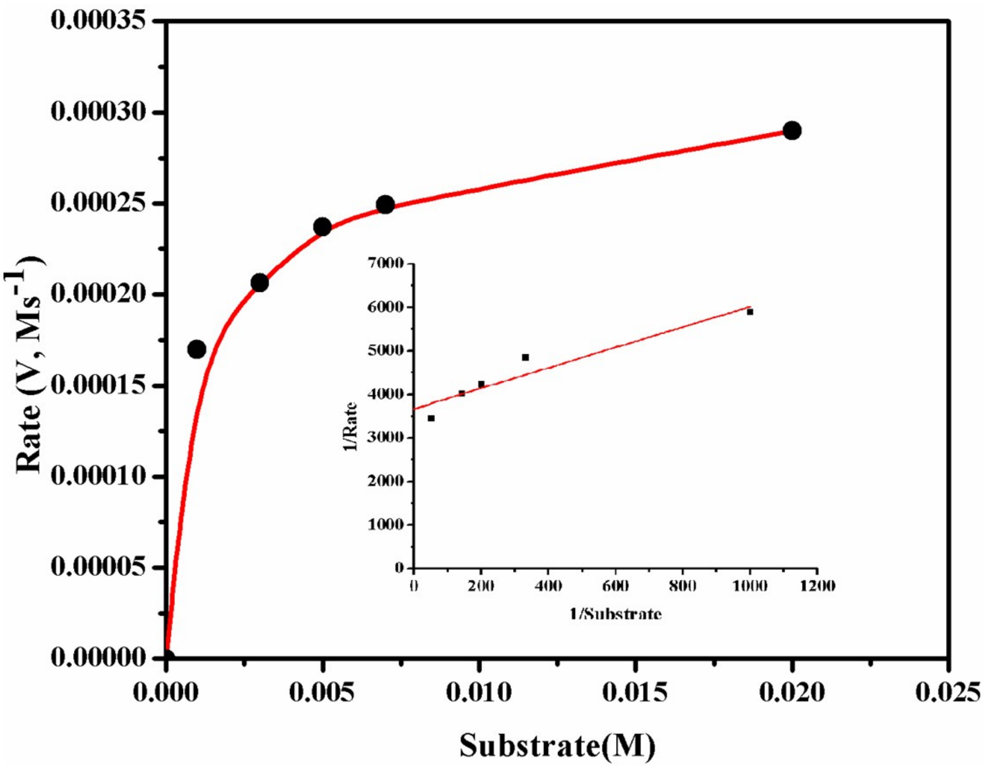

Fig. S11 Rate vs. substrate concentration plot for complex **3**; Inset: Lineweaver–Burk plot

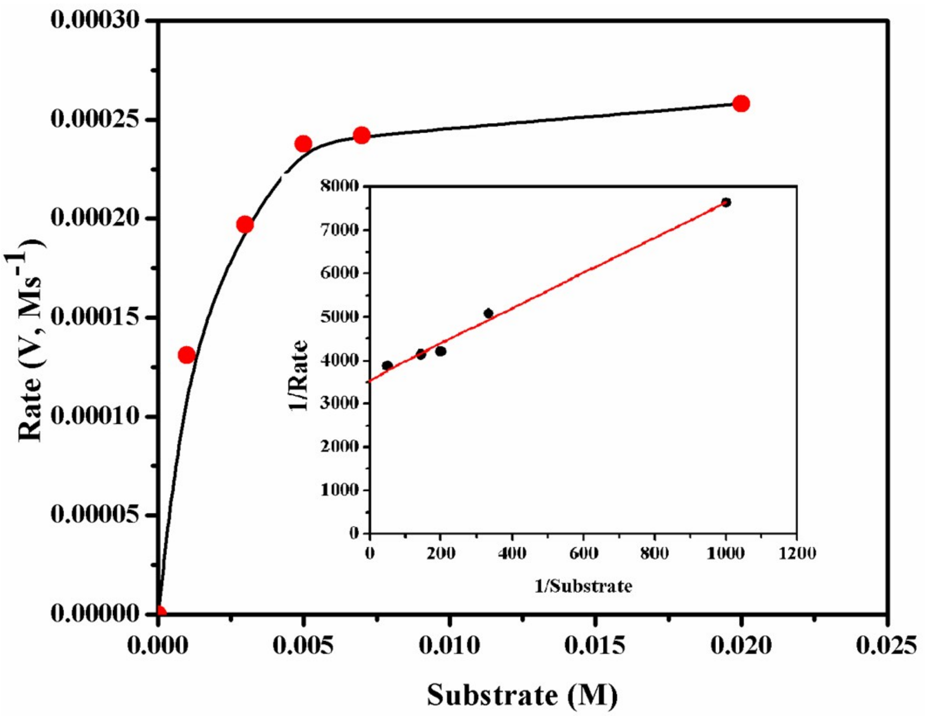

Fig. S12 Rate *vs.* [DTBC] plot for **4**; Inset: Lineweaver–Burk plot.

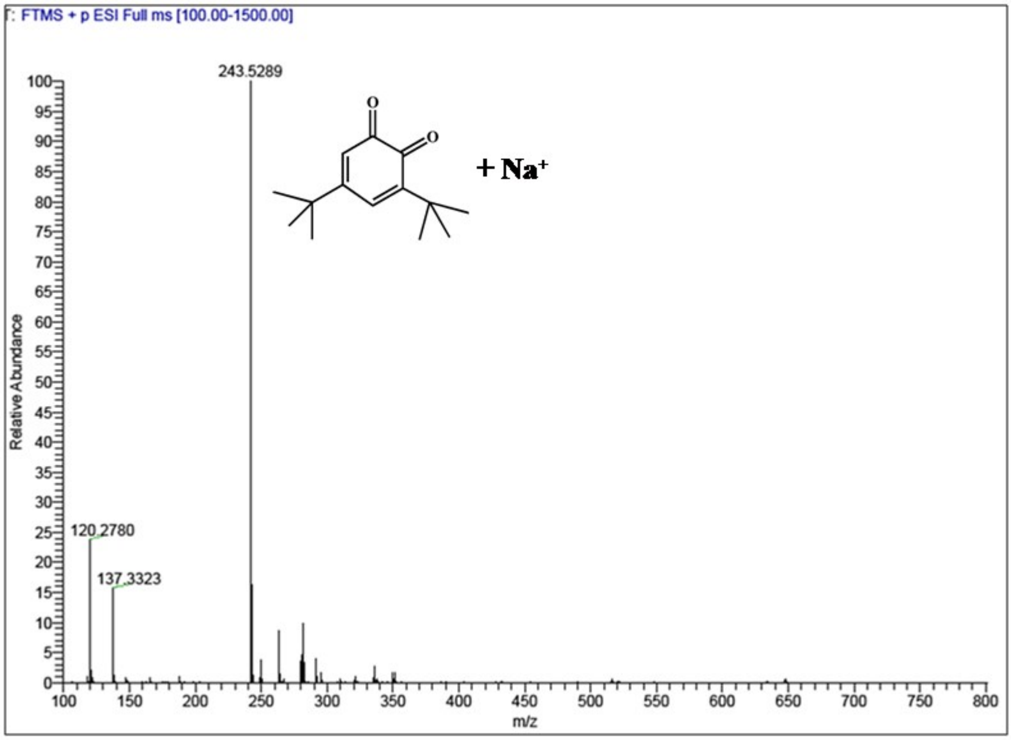

Fig. S13 ESI MS spectrum of complex 3 after addition of 3, 5-DTBC

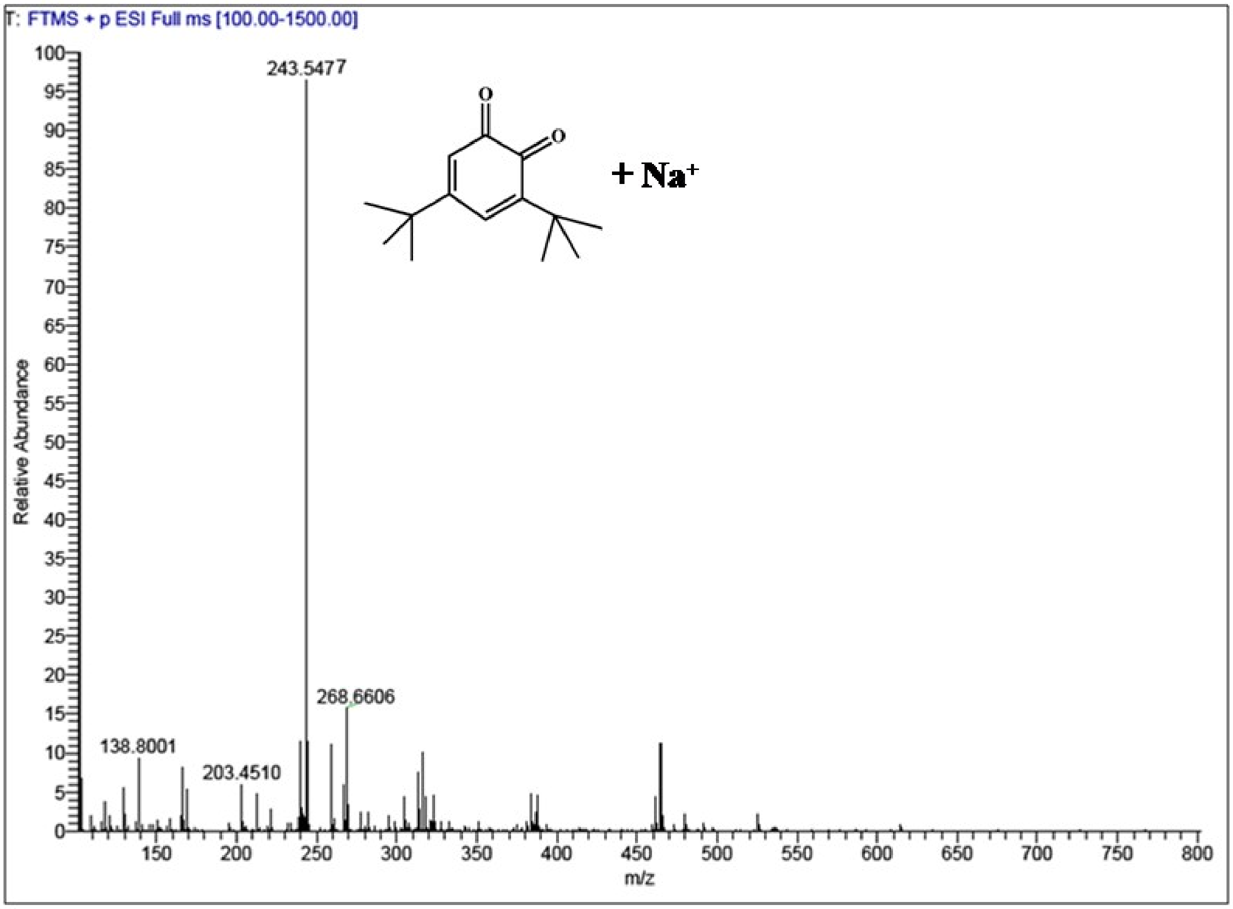

Fig. S14 ESI MS spectrum ofcomplex 4 after addition of 3, 5-DTBC

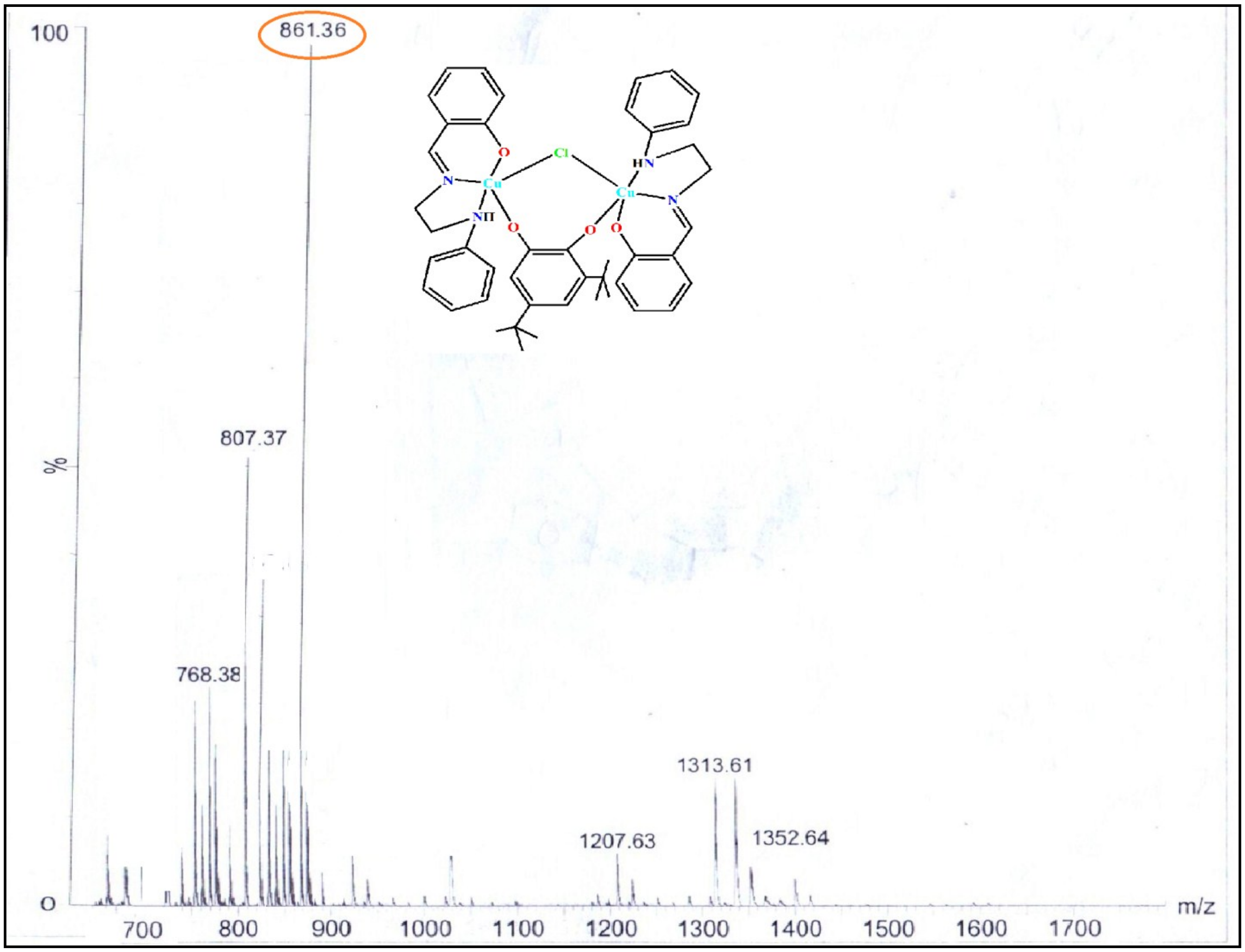

Fig. S15 ESI MS spectrum of complex **3** after addition of 3, 5-DTBC at higher m/z region.

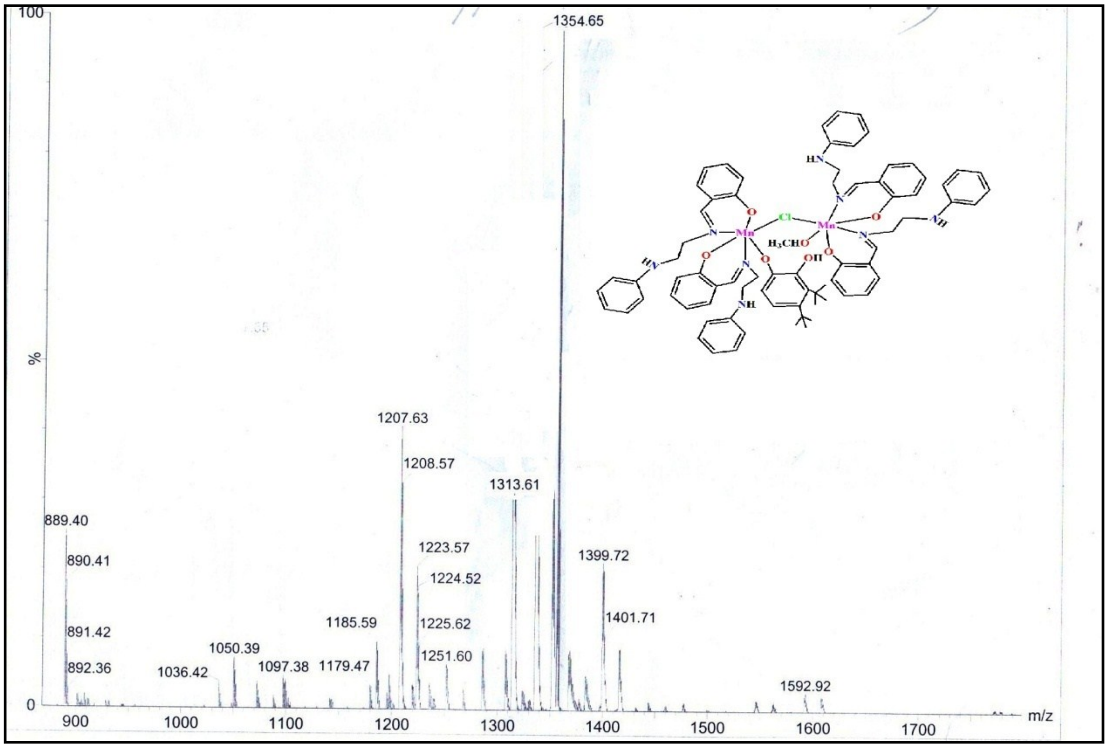

Fig. S16 ESI MS spectrum of complex **4** after addition of 3, 5-DTBC at higher region.

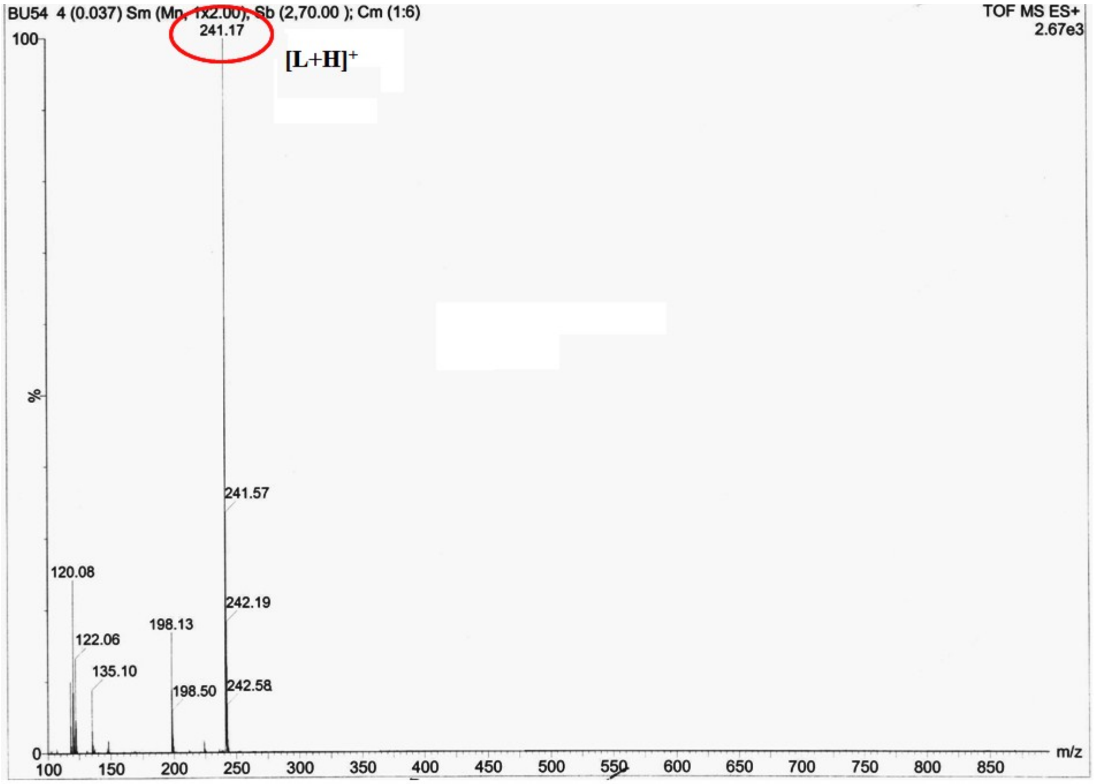

Fig. S17 ESI MS spectrum of L

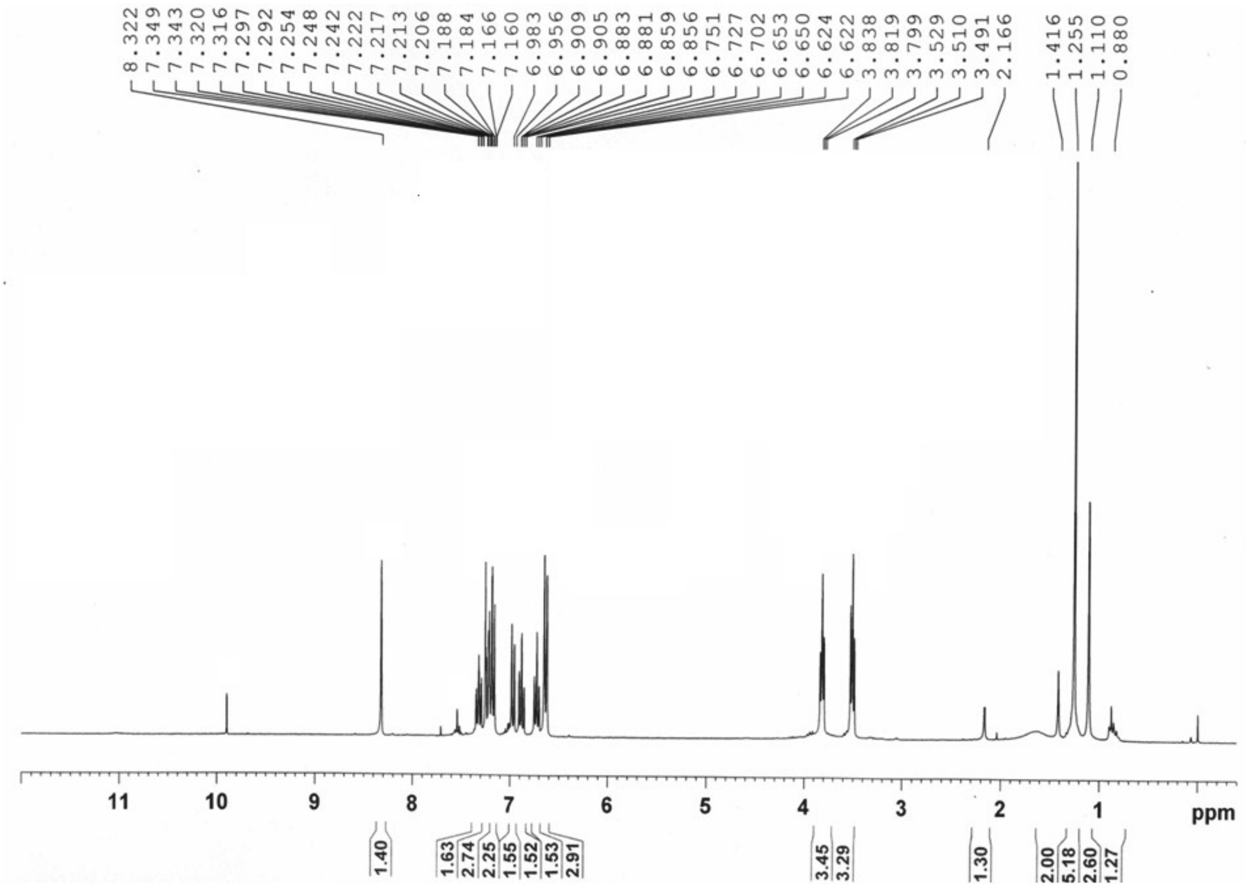

Fig. S18 ^{1}HNMR spectrum of L in $CDCl_3$

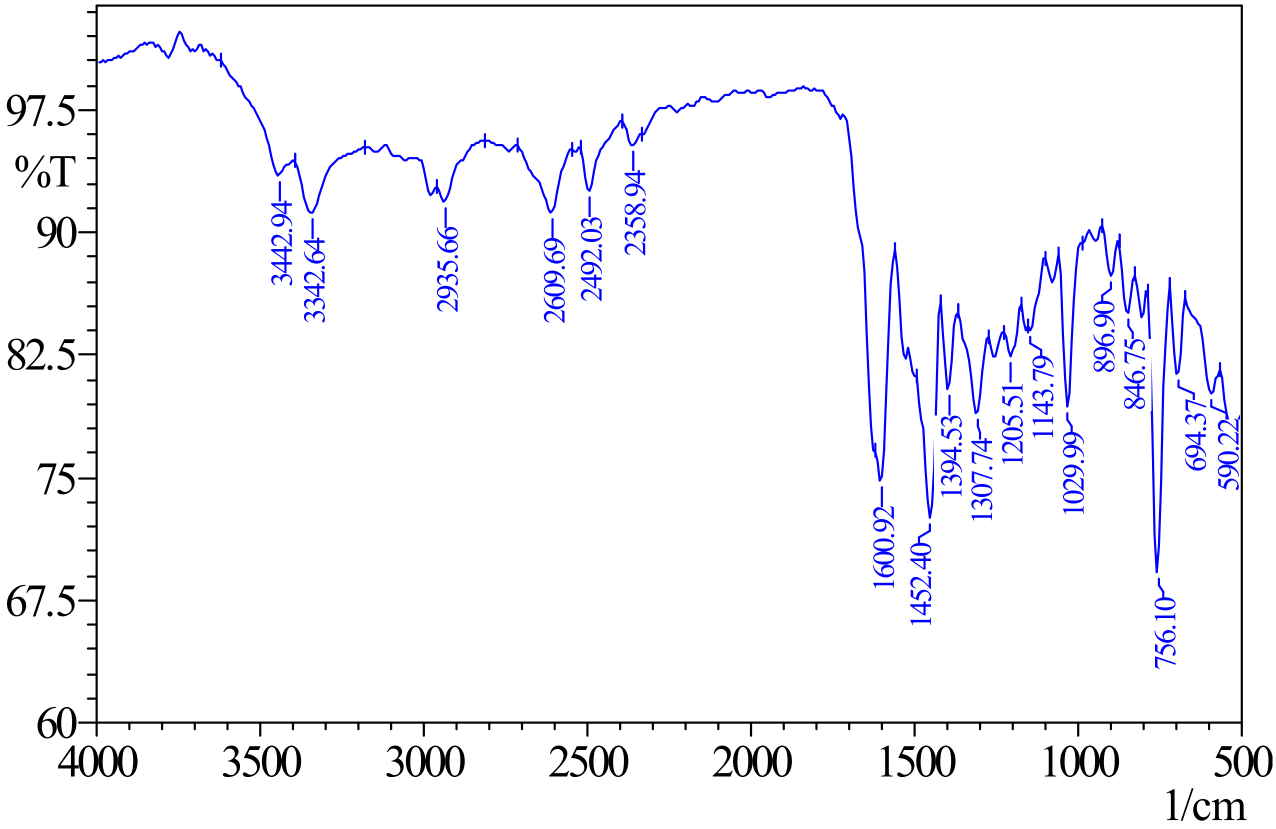

Fig. S19 FTIR spectrum of complex 3

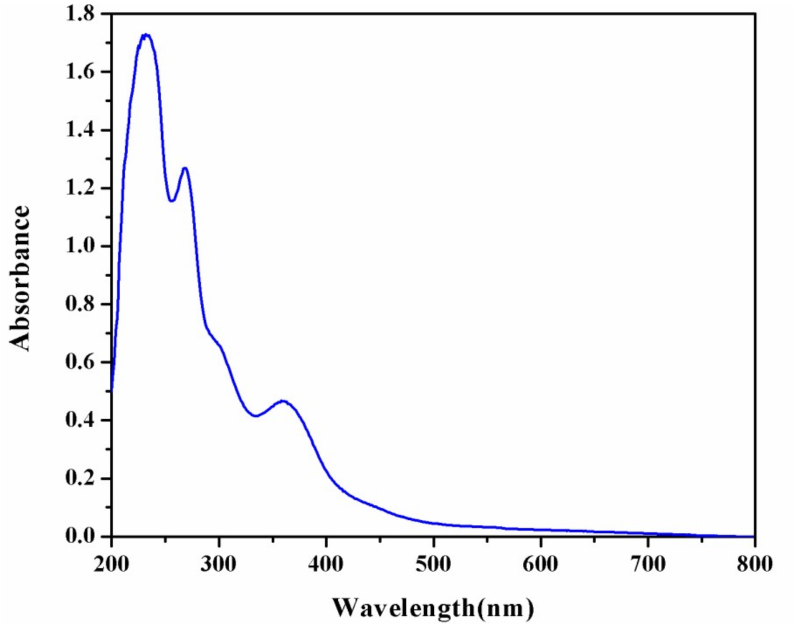

Fig. S20 Absorption spectrum of complex 3

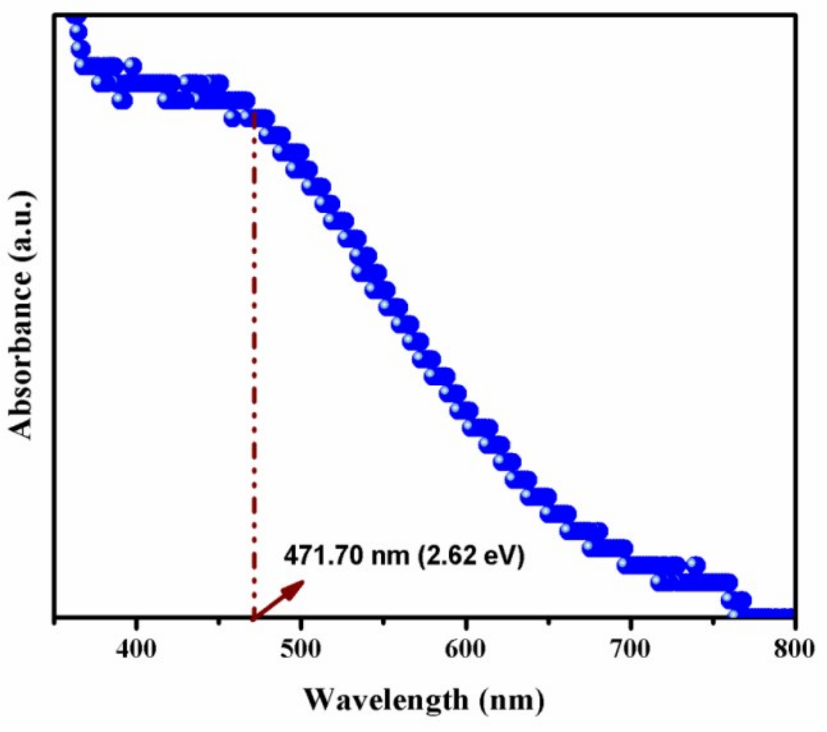

Fig. S21 The λ_{max} = 471 nm (corresponding band gap is ~ 2.62 eV). Thus, a blue shift of the band gap energy of the synthesized CuO NCs is observed to that of bulk CuO (1.2eV).[3]

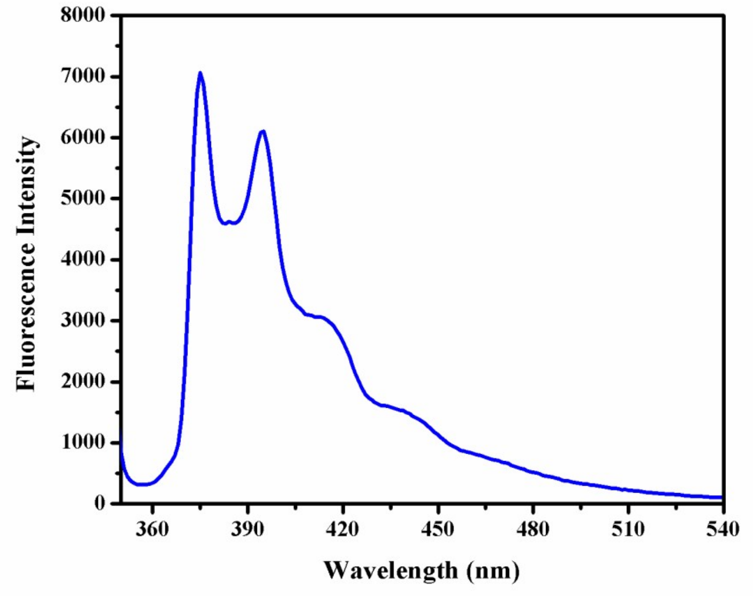

Fig. S22 Emission spectrum of CuO NCs

The room temperature photoluminescence spectrum of prepared CuO NCs is shown in Fig. S18 (λ_{Ex} = 340 nm). Four distinguishable emission peaks are observed at about 375, 395, 415 and 440 nm with different intensities for the CuO NC[4]. Two strong peaks at~375, 395 nm corresponds to the band-edge emission. The band gap corresponds to the band edge emission is ~ 3.1eV, much higher than the reported value. Two broad peaks at ~415 nm and 440 nm arises from singly ionized oxygen vacancy resulting in green emission of CuO NCs because of recombination of a photo generated hole with a singly ionized electron in valence band, also confirmed from the Rietveld refinement result.

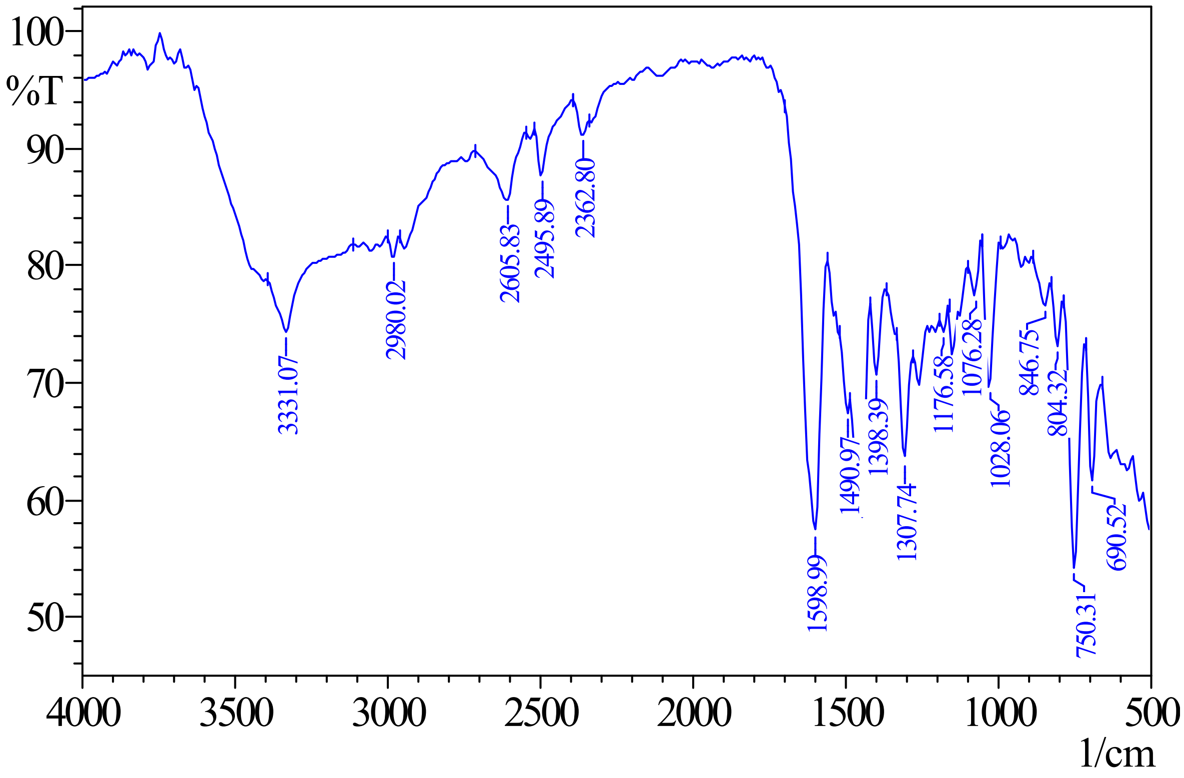

Fig. S23 FTIR spectrum of complex **4**

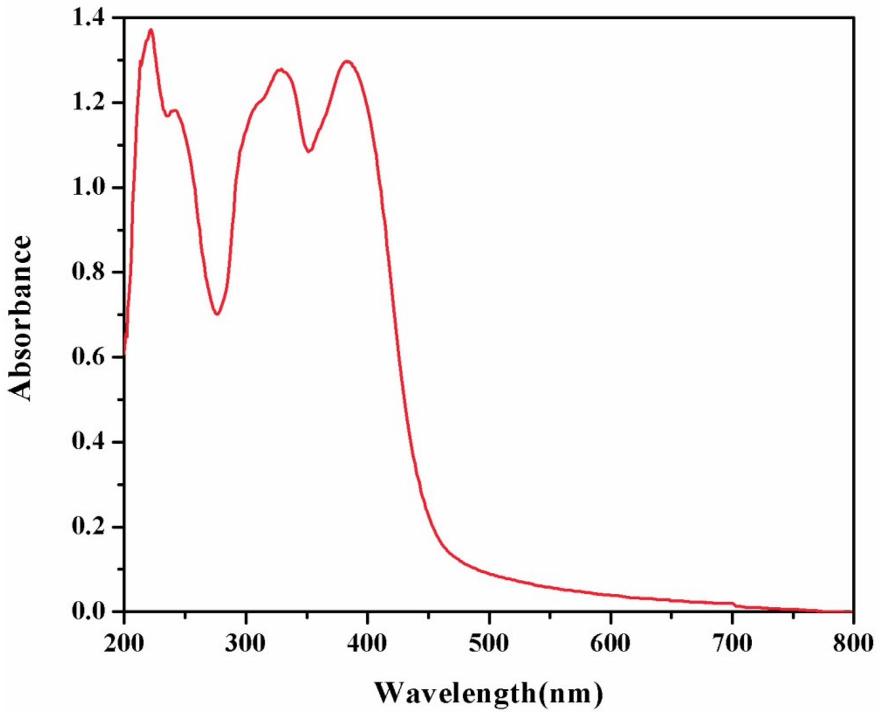

Fig. 24 Absorption spectrum of complex **4**

Table S1.Initial rates as a function of [3, 5-DTBC]; [1] = 1x10^{-4}mol dm^{-3}]

[3,5-DTBC](mol dm^{-3})	**V (mol dm^{-3} s^{-1}) of 3**	**V (mol dm^{-3} s^{-1}) of 4**
1E-3	1.699E-4	1.31E-4
3E-3	2.064E-4	1.97E-4
5E-3	2.369E-4	2.378E-4
7E-3	2.491E-4	2.42E-4
1E-2	2.899E-4	2.58E-4

Table S2 Optimization of bases

Entry	Base	Amount of base(mmol)	Yield (%)
1.	Cs_2CO_3	1.0	60
2.	K_3PO_4	1.0	21
3.	K_2CO_3	1.0	82
4	K_2CO_3	1.2	88
5.	K_2CO_3	1.3	96

Reaction condition: Iodobenzene (1.0 mmol), benzamide (1.2mmol), catalyst (10mg), 18 h, 110^0C, solvent free, GC yield

Table S3. Optimization of solvent

Entry	Solvent	Yield (%)
1.	Water	<5
2.	Dimethyl formamide	54
3.	*p*-Xylene	<5
4.	-	96

Reaction condition: Iodobenzene (1.0 mmol), benzamide (1.2mmol), K_2CO_3 (1.3 mmol), solvent (2.5mL), catalyst (10mg), 18 h, 110^0C.

Table S4 Structural and microstructural parameters of CuO NCs, from Rietveld refinement

Sample	G.O.F	Structural parameters							Microstructural parameters	
		Lattice Parameters				Atomic coordinate	Oxygen occupancy	Texture factor	Crystal size (nm)	Lattice strain
		a (Å)	b (Å)	c (Å)	β (º)					
CuO NCs	1.17	4.6825	3.4246	5.1305	99.38	0.9112	0.9525	0.8771	216.76	$1.1x10^{-3}$

Table S5.Crystal data of complex **3** and complex **4**.

Complex	**3**	**4**
Empirical formula	$C_{15}H_{15}ClCuN_2O$	$C_{30}H_{30}ClMnN_4O_2$
Formula weight	338.28	568.99
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	Pbca
T (K)	293 K	150 K
α (Å)	7.0197(3)	9.4779(8)
b (Å)	24.9592(19)	19.2235(17)
c (Å)	8.1874(6)	28.921(2)
β (º)	98.001(6)	(90)
Volume (Å^3)	1420.52(16)	5269.3(8)
Z	4	8
ρ_{calc}g/cm^3	1.582	1.434
μ. (mm^{-1})	1.721	0.638
F(000)	692.0	2372.8
Index ranges	$-8 \leq h \leq 8$, $-30 \leq k \leq 30$, $-9 \leq l \leq 9$	$-11 \leq h \leq 11$, $-24 \leq k \leq 23$, $-35 \leq l \leq 36$
Reflections collected	11403	97358
Independent reflections	2567 [R_{int} = 0.1046]	5427 [R_{int} = 0.1639]
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0783, wR_2 = 0.1508	R_1 = 0.0452, wR_2 = 0.0843
Final R indexes [all data]	R_1 = 0.1159, wR_2 = 0.1663	R_1 = 0.1234, wR_2 = 0.1115

References

1. N. Ademir, M. R. Liane, J. B. Adailton, S. Bruno, W. Clayton and S. Erineu, *Inorg. Chem.* 2002, **41**, 1788-1794.

2. P. Seth, L. K. Das, M. G. B. Drew and A. Ghosh, *Eur. J. Inorg. Chem*. 2012, 2232–2242.

3. E.P. Kirby and R.F. Steiner, *J. Phys. Chem.,* 1970, **74** (26) 4480.

4. A. Bhattacharjee and M. Ahmaruzzaman,*RSC Adv.*, 2016, **6**, 41348-41363.