Supporting Information
For

Ligand Assisted Electrocatalytic Water Oxidation by a Copper (II) Complex in Neutral Phosphate Buffer

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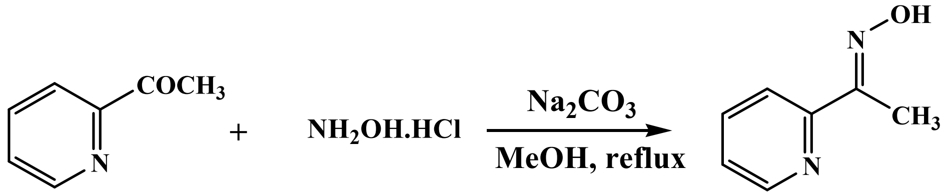
Experimental Procedures:

All reagents and solvents were purchased from commercial sources and were of reagent grade. UV-visible spectra were taken on Cary-60 UV-visible spectrophotometer. FT-IR spectra were taken on a Cary 630 spectrophotometer with sample prepared as KBr pellets. ^{1}H-NMR spectra was obtained with a 400MHz Varian FT-spectrometer. Chemical shifts (δppm) were referenced either with an internal standard (Me_4Si) for organic compounds or to the residual solvent peaks.The X-band Electron Paramagnetic Resonance (EPR) spectra of the complex were recorded on a JES-FA200 ESR spectrometer. The magnetic moment of the complex were measured on a Cambridge magnetic balance. Conductivity measurements were recorded using a Eutech instrument CON 700. Electrochemical measurements were made using a CH Instruments 6035A potentiostat. A glassy carbon working electrode, Pt wire auxiliary electrode, and a Ag/Ag^+ reference electrode were used in a three-electrode configuration.Mass spectra of the compounds were recorded in a Waters Q-Tof Premier and Aquity instrument. FESEM was performed on a Zeiss microscope; SUPRA 55VP-Field Emission Scanning Electron Microscope. EDAX was performed on a Zeiss X-ray analyser; SUPRA 55VP-Field. The coating was done with Platinum before the experimental analysis.

A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a crystal mounting loop with paratone oil. The single crystal data were collected on a BRUKER AXS (D8 Quest System) X-ray diffractometerequipped with PHOTON 100 CMOS detector at 293(2) K. The X-ray generator was operated at 50 kV and 30 mA using Mo Kα ($\lambda = 0.71073$ Å) radiation. The unit cell measurement, data collection (φ and ω scan), integration, scaling and absorption corrections for the crystals of both complexes was done using Bruker Apex II software.[1]Data were collected with ω scan width of 0.5°. Sufficient numbers of frames were collected for different setting of φ keeping the sample-to-detector distance fixed. The data were reduced using SAINTPLUS,[2] and an empirical absorption correction was applied using the SADABS program.[3] The structure was solved and refined using SHELXL97[4] present in the WinGx suit of programs (Version 1.63.04a).[5] All the hydrogen positions were initially located in the difference Fourier maps, and for the final refinement, the hydrogen atoms were placed in geometrically ideal positions and refined in the riding mode. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against $|F^2|$ was carried out using the WinGx package of programs.[5]The hydrogen atoms of the coordinated and the lattice water were fixed using Olex2 1.2 package of programs.[6,7]Structural illustrations have been drawn with ORTEP-3 for Windows. Details of the structure solution and final refinements for the compoundsare given in Table S1. CCDC:1879870 contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.Structural illustrations have been drawn with ORTEP-3 for Windows.

Preparation of Ligand (L_1H):



Scheme 1.

Acetylpyridine (1g, 8.2 mmol) was dissolved in 25mL of methanol. To it hydroxylamine hydrochloride (0.63, 9.0 mmol), dissolved in methanol was added. To the reaction mixture, sodium carbonate (1.3g, 1.22 mmol)was added. The reaction mixture was refluxed for 1.5hat 60 °C. After the completion of the reaction, the reaction mixture turns light pink. The reaction mixture was then filtered and the filtrate was kept for crystallization. The white crystals obtained were dried and weighed.Yield: 0.930g (~84 %).

UV-visible (methanol): λ_{max}, 204 nm (ε = 5573 M^{-1} cm^{-1}), 240 nm (ε = 4614 M^{-1} cm^{-1}), 273 nm (ε = 5410 M^{-1} cm^{-1}).

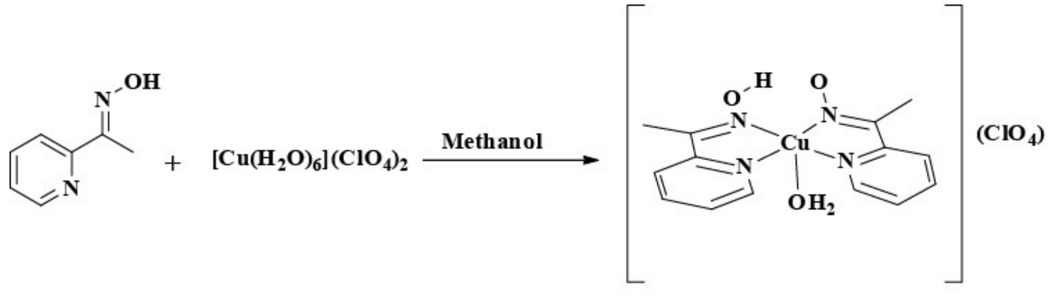
FT-IR (KBr pellet): 3178, 2846, 1594, 1490, 1438, 1000, 933, 829, 785, 681 cm^{-1};

^{1}H-NMR (400 MHz, CD_3COCD_3): $\delta_{ppm,}$10.58, 8.55, 7.87, 7.29, 2.90, 2.27.

^{13}C-NMR (100 MHz, CD_3COCD_3): $\delta_{ppm,}$154.97, 148.78, 136.06, 123.41, 119.87, 87.22, 9.36.

Mass: $(m+H^+)/z$: Calcd. 137.06; Found, 137.07.

Synthesis of complex 1, $[Cu(L_1H)(L_1)(H_2O)](ClO_4)$:



(Complex 1)

Scheme 2.

Copper(II) perchlorate hexahydrate, $[Cu(H_2O)_6](ClO_4)_2$ (0.68g, 1.8 mmol)was dissolved in 25 ml methanol and to this blue solution, the ligand **L_1H**(0.5g, 3.6 mmol), was added drop wise. The color of the solution changes from blue to dark green. The resulting mixture was stirred for 1h. Then the volume of the solution was reduced to ~10 ml. It was then kept for crystallization at room temperature which resulted into green crystalline compounds.Yield: 0.68g (~79%).

UV-visible (methanol): λ_{max}, 580 nm (ε = 138M^{-1} cm^{-1}).

FT-IR (KBr pellet): 3505, 1607, 1472, 1139, 1087, 779, 616 cm^{-1}.

Molar conductance: 117 Scm^{2}mol^{-1}.Magnetic moment:1.7 BM.

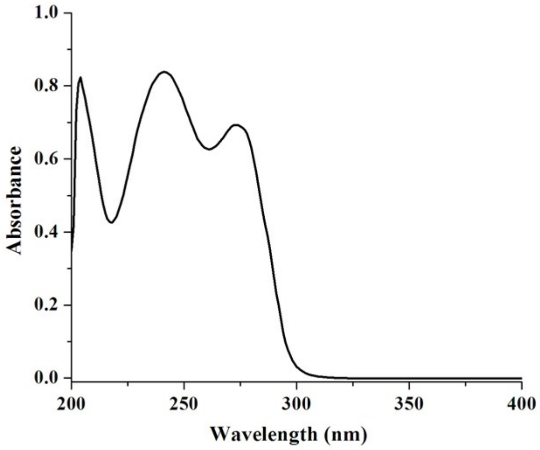


Figure S1. UV-visible spectrum of **L$_1$H** in methanol

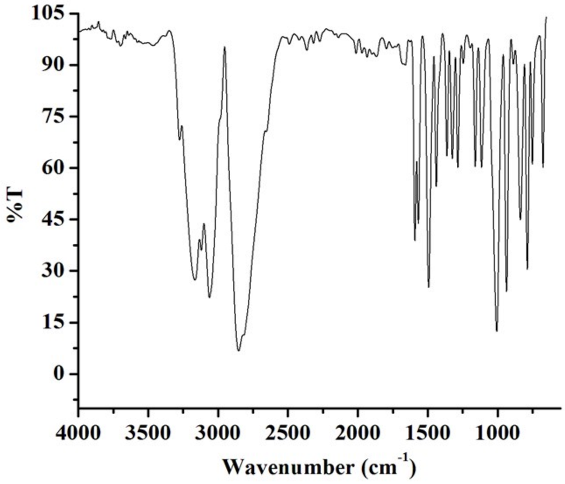


Figure S2. FT-IR spectrum of **L$_1$H** in KBr.

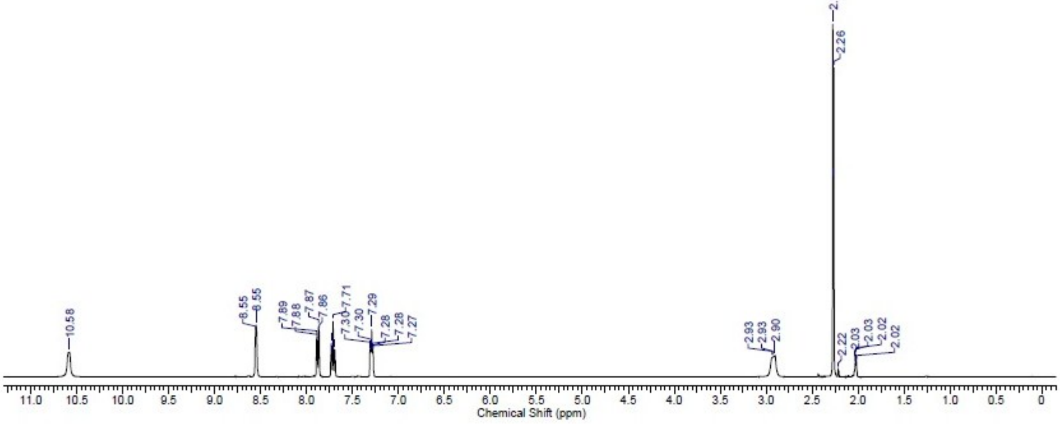


Figure S3.^{1}H-NMR of **L$_1$H** in CD$_3$COCD$_3$

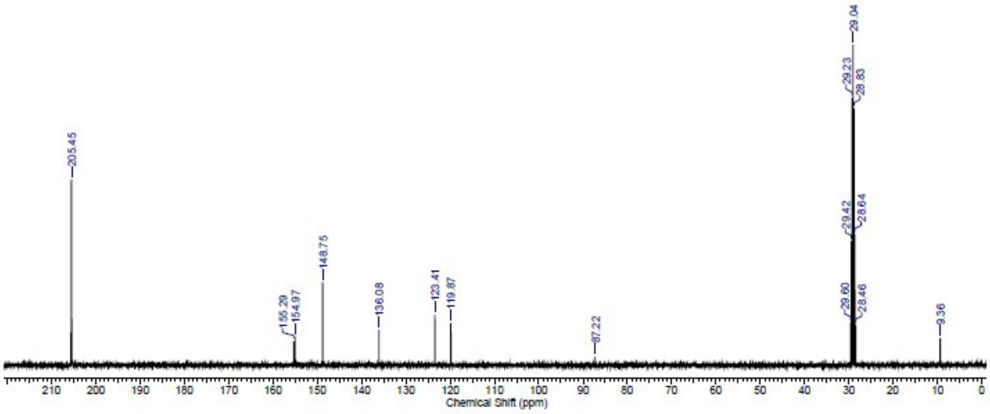
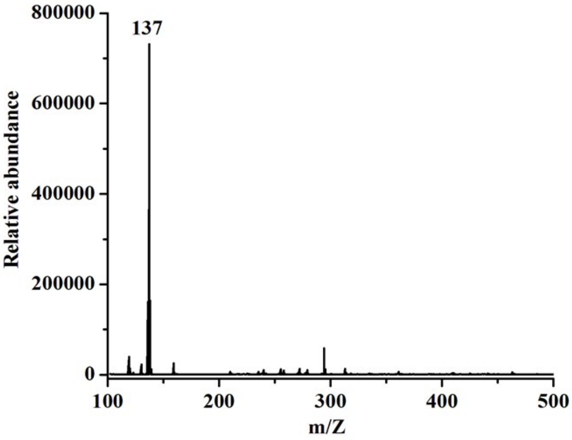
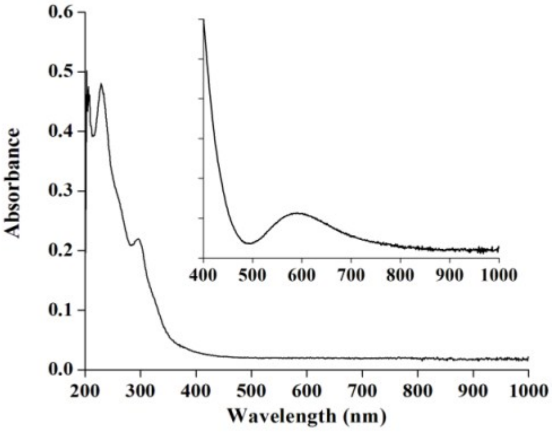


Figure S4.^{13}C-NMR of **L_1H** in CD_3COCD_3



FigureS5.ESI-Mass spectrum of the **L_1H** in methanol



FigureS6. UV-visible spectrum of complex **1** in 0.1 M neutral phosphate buffer. The inset shows a magnified view of the 400-1000 nm region.

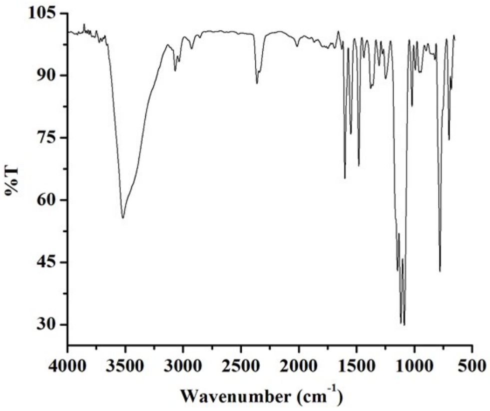


Figure S7.FT-IR spectrum of complex **1** in KBr.

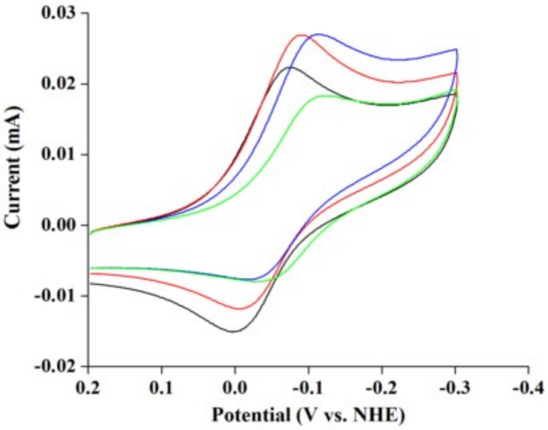


Figure S8. Cyclic voltammogram of complex **1** recorded in the range 0 to -0.5 V vs. Ag^+/Ag reference electrode at different pH. (Black, red, blue, green line at pH 6.8, 7, 7.4, and 7.8 respectively)

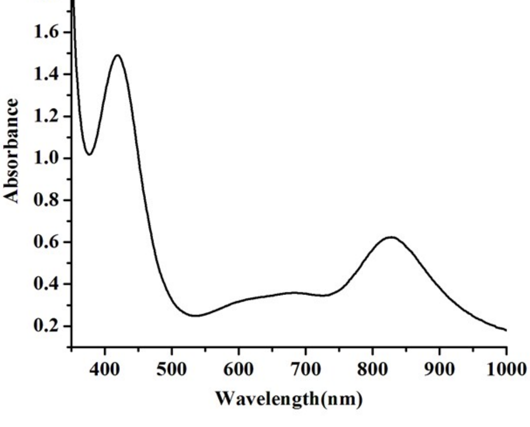


Figure S9.UV-visible spectra of complex **1** after electrolysis at +0.66 V in neutral phosphate buffer at room temperature.

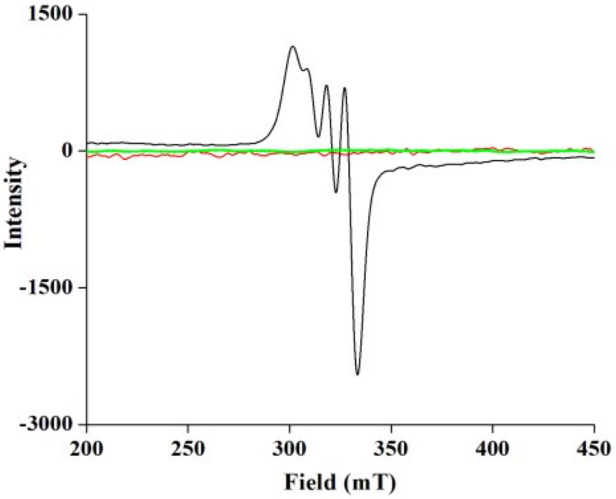


Figure S10. X-band EPR spectra of complex **1** (black line) and after electrolysis at +0.64 V (red line) and +0.93 V (green line).

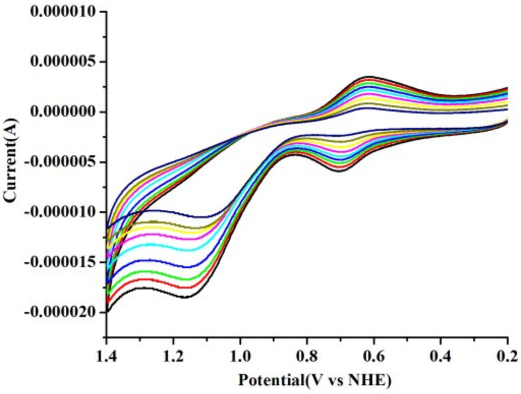


Figure S11. Cyclic voltammogram (Background corrected) of complex **1** recorded in the range 0 to 1.2 V vs. Ag^+/Ag reference electrode at different scan rate. (dark blue, grey, yellow, pink, light blue, navy blue, green, red, black line at 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV/sec respectively)

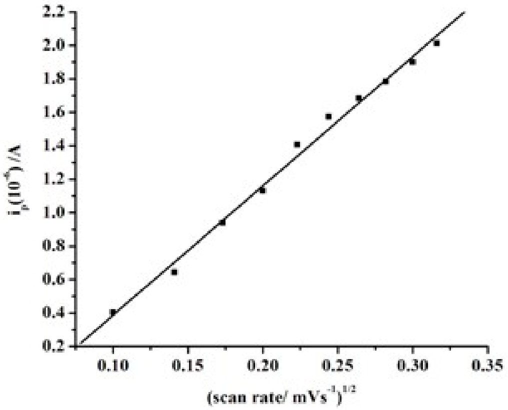


Figure S12. Dependence of the peak current (background subtracted) for the Cu^{II}/Cu^{I} couple of complex **1** on the square root of scan rate with standard three electrode system in 0.1 M pH 7 phosphate buffer.

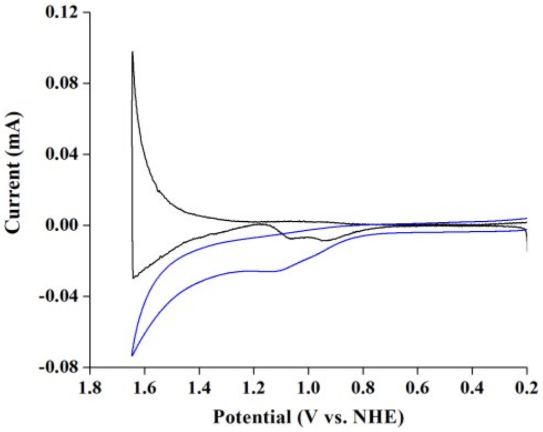


Figure S13. Cyclic voltammogram of Zn^{2+}-complex of L_1H (blue) and its first derivative plot (black) in neutral phosphate buffer recorded in the range 0 to 1.45 V with a glassy carbon (GC) working electrode, a Ag/AgCl reference electrode and a Pt counter electrode, scan rate 100 mV s^{-1}

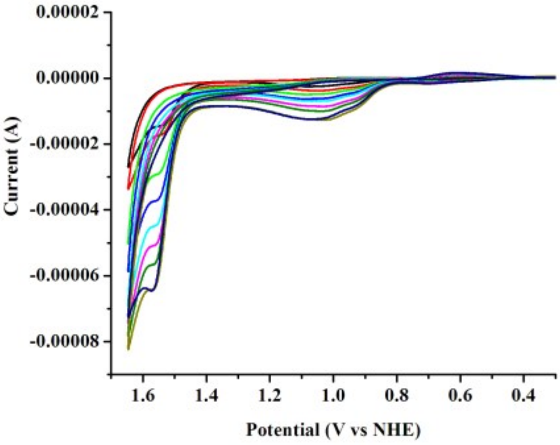


Figure S14. Background corrected CV of complex **1** at 0.05 (black), 0.07 (red), 0.14 (green), 0.18 (blue), 0.22 (cyan), 0.26 (magenta), 0.34 (olive), 0.38 (dark yellow) and 0.42 mM (navy) concentration in 0.1 M neutral phosphate buffer. Scan rate: 100mV/s.

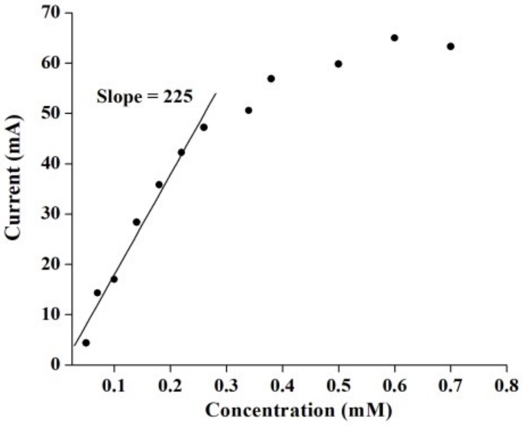


Figure S15. Catalytic current at 1.49 V as a function of the catalyst concentration from 0.05 to 0.7 mM measured in 0.1 M neutral phosphate buffer.

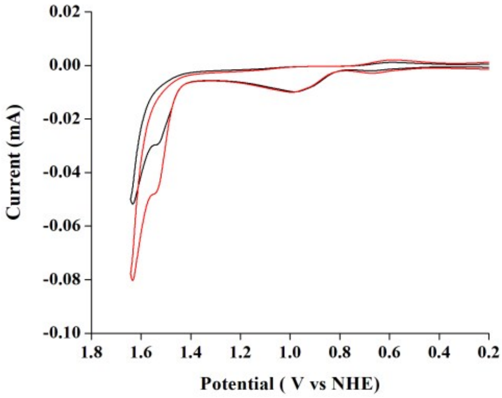
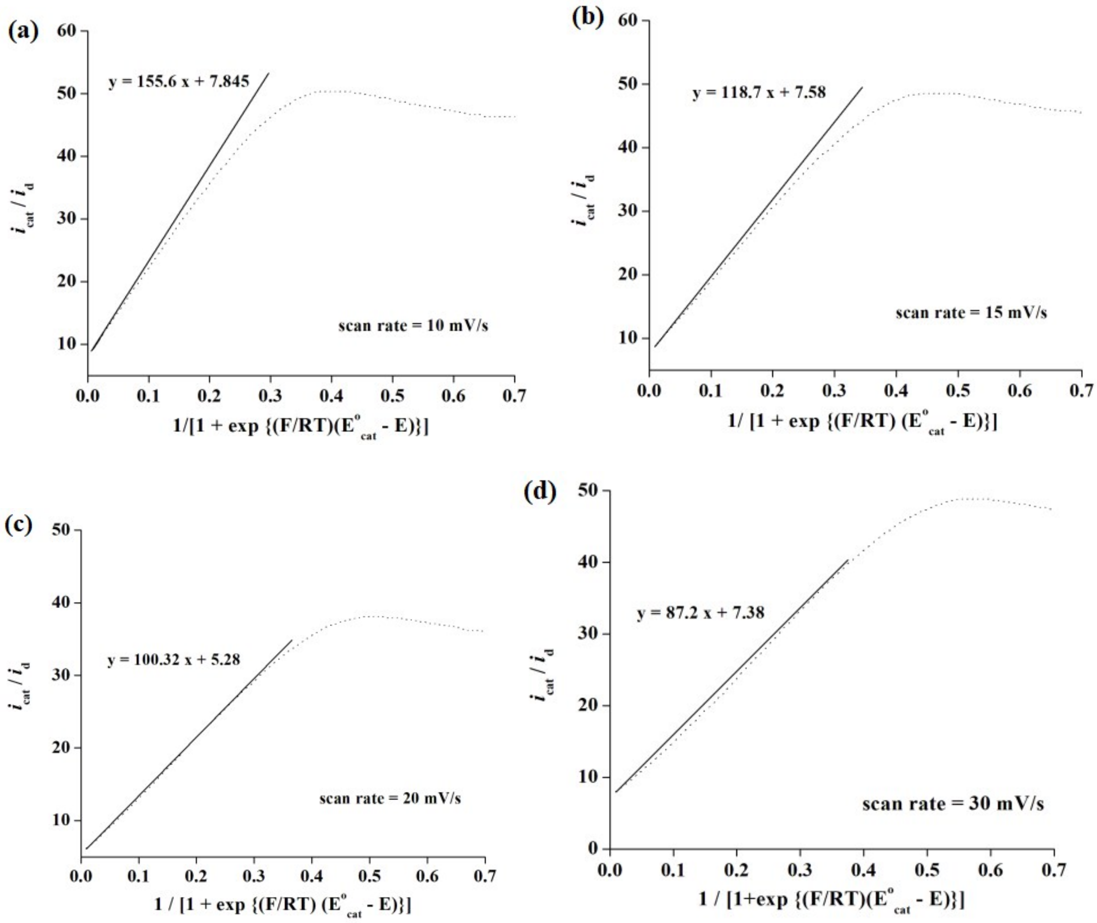


Figure S16. CV curves of complex **1** in H_2O (Red) and D_2O (Black) phosphate buffer with glassy carbon as working electrode at a scan rate 100 mV/s.



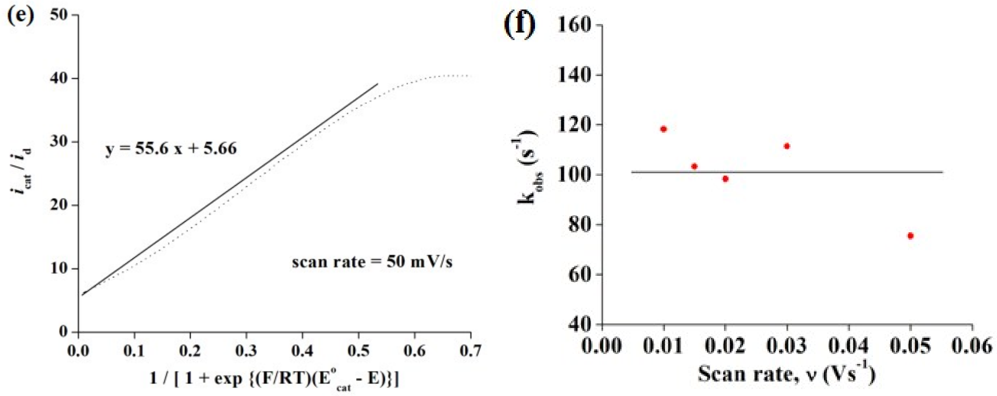


Figure S17. (a) to (e) FOWA. (f) Plot of the different k_{obs} values extracted from the foot-of-the-wave analysis at scan rate 10-50 mVs^{-1}. In figure (f) the black line represents the average k_{obs} value (~100 s^{-1}).

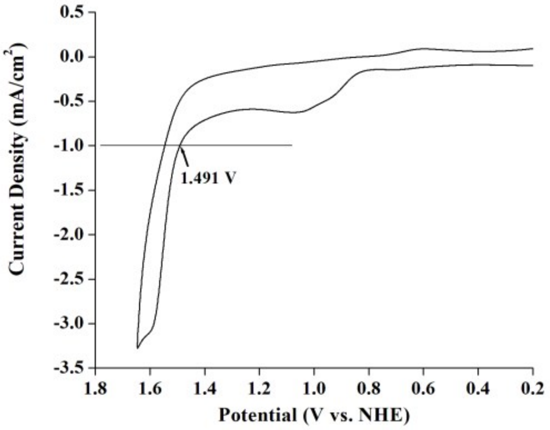


Figure S18. CV of 1mM solution of complex **1** in 0.1 M neutral phosphate buffer at 100mV/sec scan rate. The current density of 1mA/cm^{2}was obtained at 1.491 V.

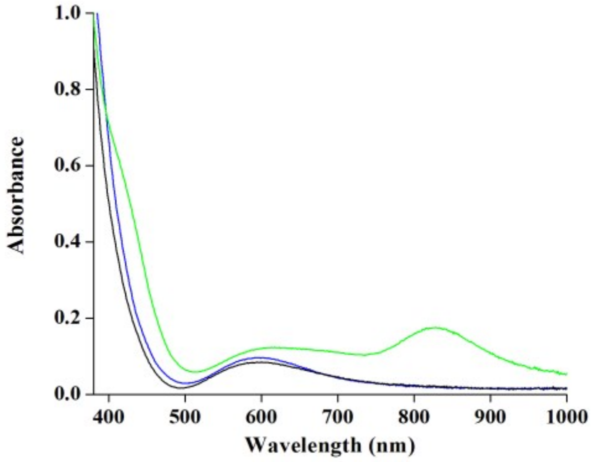


Figure S19.UV-visible spectra of complex **1** before electrolysis (blue), just after completion of electrolysis (green) and after 1hr of completion of electrolysis (black) at 1.55 V vs. NHE in 0.1 M neutral phosphate buffer.

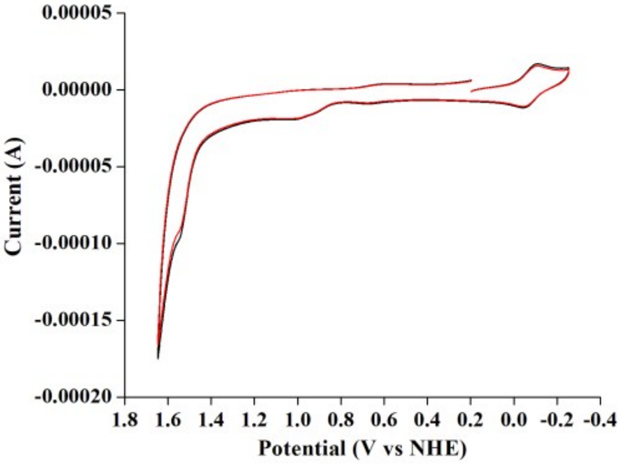


Figure S20. Cyclic voltammogram of complex **1** before (black) and after electrolysis (red) at 1.55 V vs. NHE in 0.1 M neutral phosphate buffer with a glassy carbon (GC) working electrode (area 0.07 cm^2), a Ag/AgCl reference electrode and a Pt counter electrode, scan rate 100 mV s^{-1}.

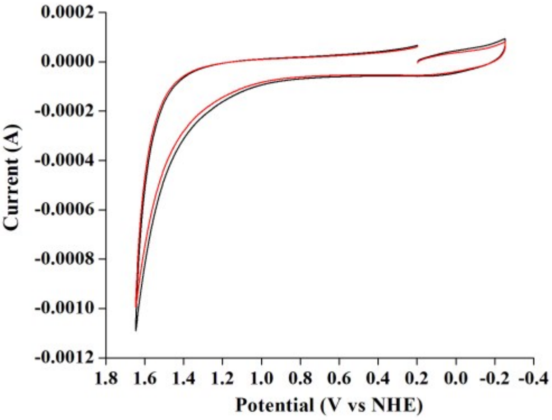


Figure S21. Cyclic voltammogram recorded in 0.1 M neutral phosphate buffer in absence of complex **1** with fresh (black) and used (red) ITO working electrode (area 4 cm^2), a Ag/AgCl reference electrode and a Pt counter electrode, scan rate 100 mV s^{-1}.

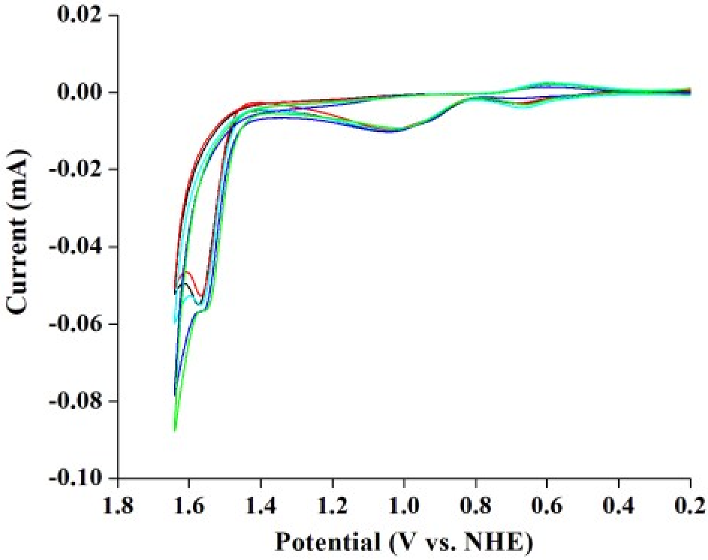
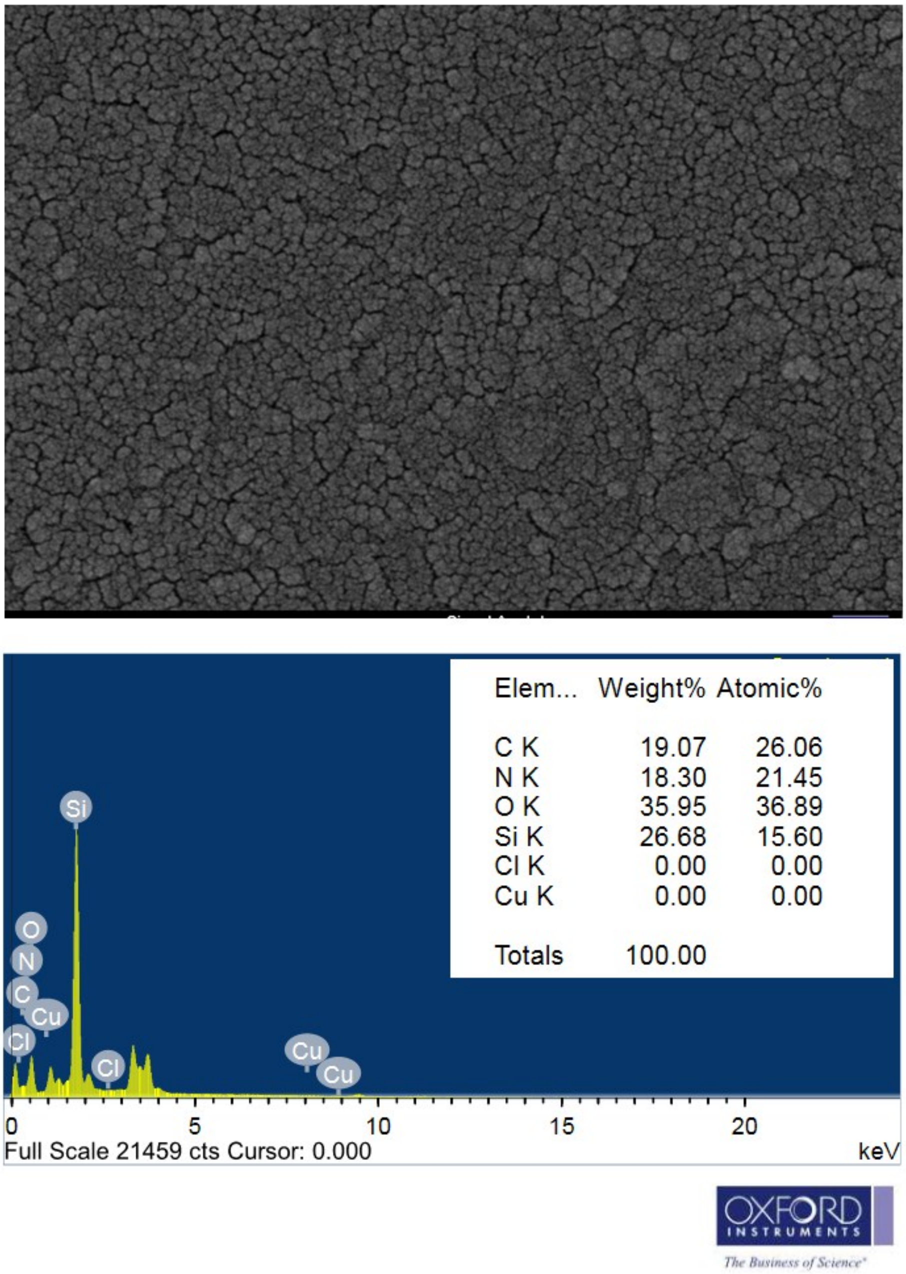
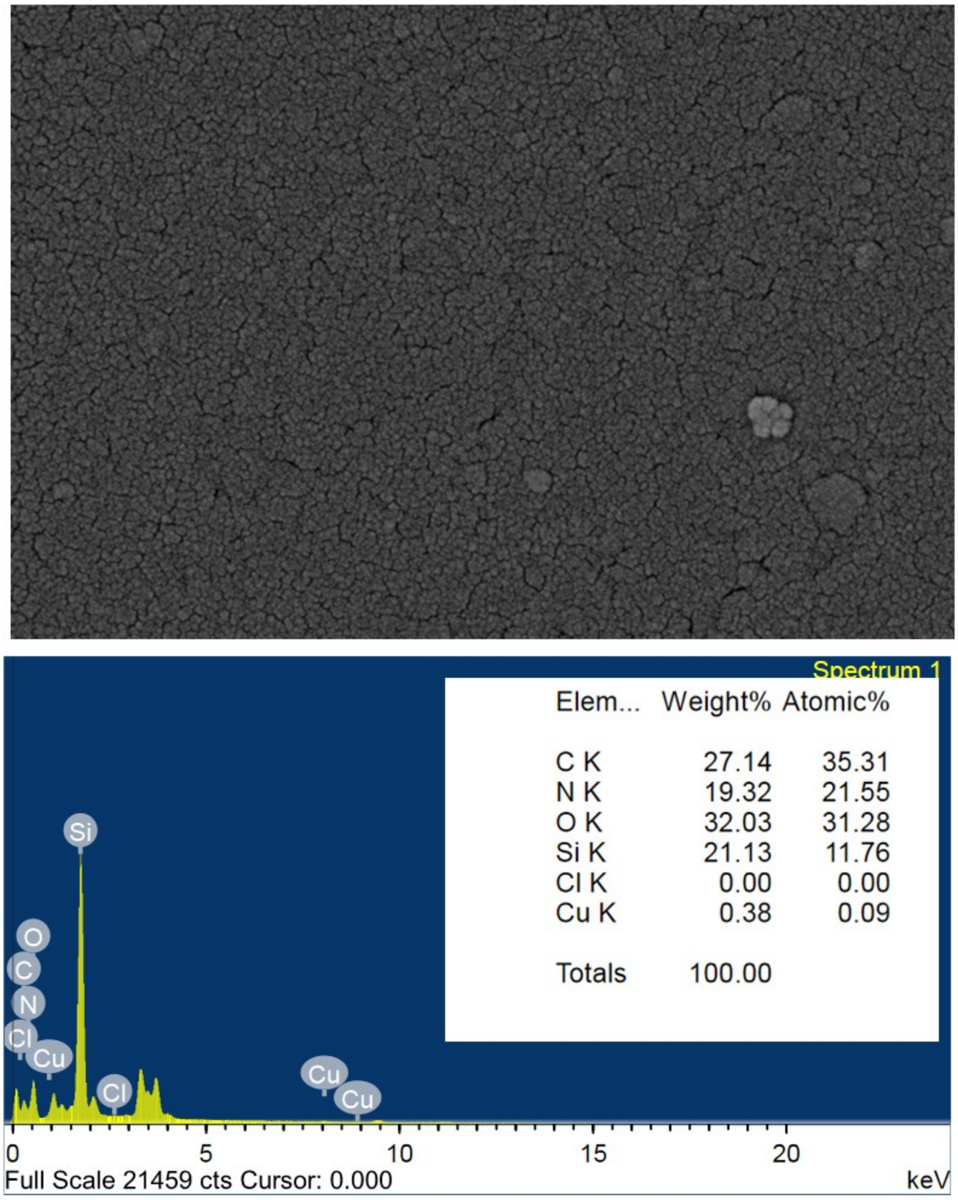


Figure S22. Background corrected cyclic voltammogram of 0.5 mM solution of complex **1** in 0.02 M (black), 0.04 M (red), 0.08 M (cyan), 0.1 M (blue) and 0.12 M (green) neutral phosphate buffer with a glassy carbon (GC) working electrode, a Ag/AgCl reference electrode and a Pt counter electrode, scan rate 100 mV s^{-1}.



Elem...	Weight%	Atomic%
C K	19.07	26.06
N K	18.30	21.45
O K	35.95	36.89
Si K	26.68	15.60
Cl K	0.00	0.00
Cu K	0.00	0.00
Totals	100.00	

Figure S23. FE-SEM and EDX plot of fresh ITO (before electrolysis experiment) sample.



Elem...	Weight%	Atomic%
C K	27.14	35.31
N K	19.32	21.55
O K	32.03	31.28
Si K	21.13	11.76
Cl K	0.00	0.00
Cu K	0.38	0.09
Totals	100.00	

Figure S24. FE-SEM and EDX plot of used ITO (after electrolysis experiment) sample.

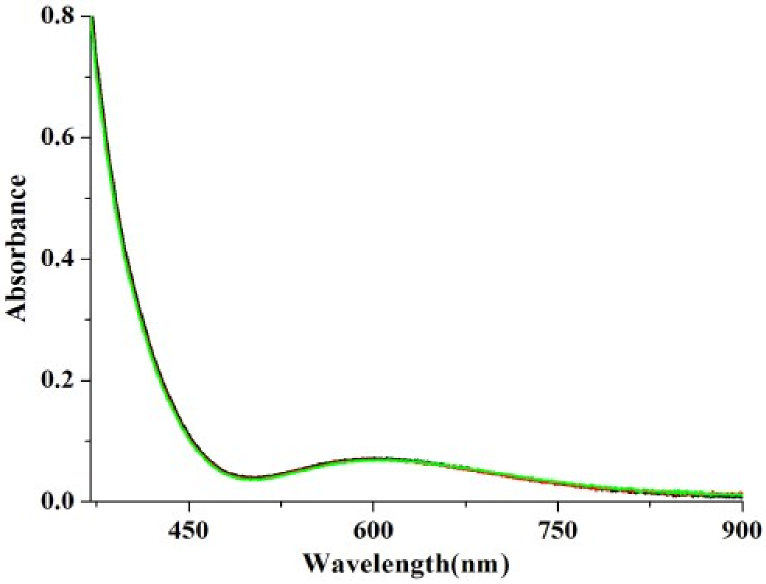


Figure S25. UV-visible spectra of freshly prepared 0.5 mM solution of complex **1** (black line) in neutral phosphate buffer and UV-visible spectra recorded after 24 hr (red line) and 48 hr (green line) with the same solution.

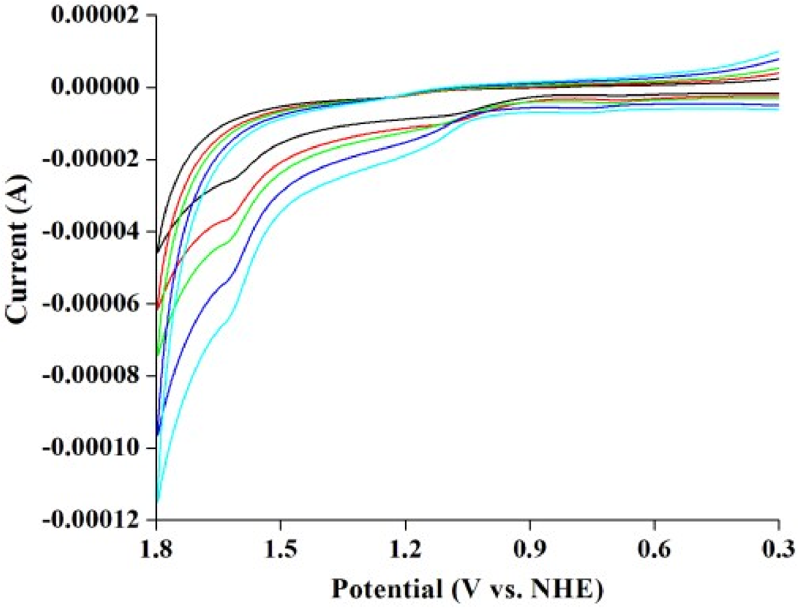


Figure S26. a) Background-corrected CVs of complex **1** in 0.1 M potassium nitrate solution at 10 (black), 15 (red), 20 (green), 30 (blue) and 40 (cyan) mVs^{-1} scan rates with a glassy carbon (GC) working electrode, a Ag/AgCl reference electrode and a Pt counter electrode.

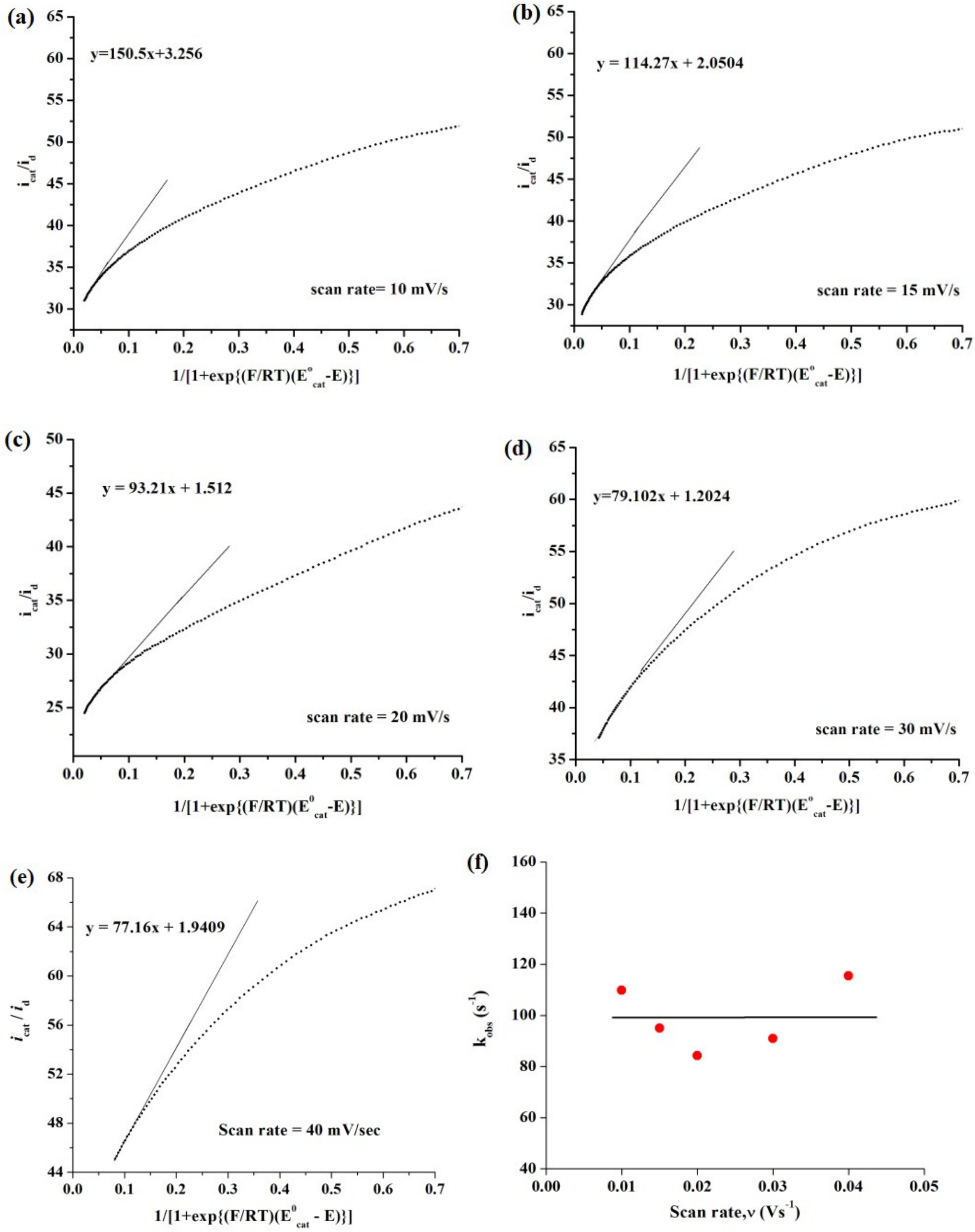


Figure S27. (a) to (e) Foot-of-the-wave analysis from cyclic voltammogram of complex **1** recorded in 0.1 M potassium nitrate solution at 10, 15, 20, 30 and 40 mVs^{-1} scan rate. (f) Plot of the different k_{obs} values extracted from the foot-of-the-wave analysis at scan rate 10-40 mVs^{-1}. In figure (f) the black line represents the average k_{obs} value (~100 s^{-1}).

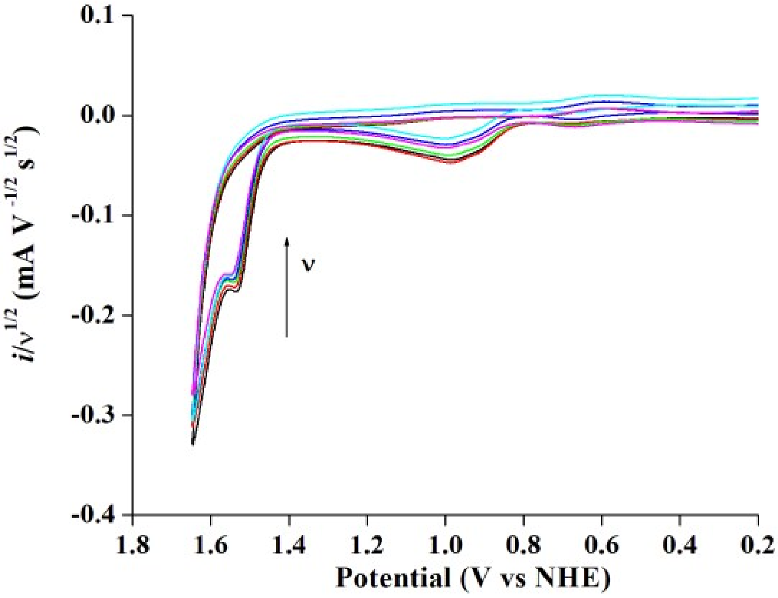


Figure S28. Cyclic voltammograms of complex **1** with currents normalized to the square root of the scan rates (50-100 mVs^{-1}) measured in 0.1 M neutral phosphate buffer.

Table S1. Crystallographic data for complex **1**

	Complex **1**
Formulae	$C_{14}\ H_{19}\ Cl\ Cu\ N_4\ O_8$
Mol. wt.	470.32
Crystal system	Monoclinic
Space group	P c
Temperature /K	293(2)
Wavelength /Å	0.71073
a /Å	6.3558(16)
b /Å	15.728(4)
c /Å	9.829(3)
α/°	90.00
β/°	101.217(7)
Ɣ/°	90.00
V/ Å^3	963.8(4)
Z	2
Density/Mgm^{-3}	1.621
Abs. Coeff. /mm^{-1}	1.322
Abs. correction	None
F(000)	482
Total no. of reflections	3000
Reflections, *I* > *2σ(I)*	2637
Reflections collected / unique	8699 / 2896
R(int)	0.0394

Data / restraints / parameters	2896 / 2 / 257
Min. 2θ/°	2.48
Max. 2θ/°	24.25
Ranges (h, k, l)	-7<= h <=7 -18<= k <=16 -11<= l <= 11
Complete to 2θ (%)	98.9 %
Refinement method	Full-matrix least-squares on F^2
Goof (F^2)	1.058
R indices [$I > 2\sigma(I)$]	R1 = 0.0496, wR2 = 0.1148
R indices (all data)	R1 = 0.0687, wR2 = 0.1236

Table S2. Important H-bonding interactions observed in complex 1

D – H … A	D – H, (Å)	H … A, (Å)	D … A, (Å)	D – H … A, (°)
O(1) --H(1B) ..O(8)#a	0.85	1.86	2.680(11)	161
O(3) --H(3A) ..O(2)	0.82	1.62	2.415(9)	164
O(8) --H(8B) ..O(5)	0.85	2.37	3.14(2)	150

Symmetry transformations used to generate equivalent atom: #a x ,y, 1+z

Table S3. Catalytic current recorded for complex **1** in different concentration of phosphate buffer.

Concentration of Sodium Phosphate Buffer used	Catalytic current (mA) at 1.55 V (vs. NHE)
0.02 M	0.005039
0.04 M	0.005002
0.08 M	0.005098
0.10 M	0.004915
0.12 M	0.005076

References:

1. Apex2, Version 2 User Manual, M86-E03078, Bruker Analytical X-Ray Systems Madison, WI, **2010**.
2. SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL, Bruker AXS Inc., Madison, Wisconsin, USA, **2004**.
3. Sheldrick, G. M. *Siemens area correction absorption correction program, University ofGöttingen, Göttingen, Germany,* **1994**.

4. Sheldrick, G. M. *SHELXL-97 program for crystal structure solution and refinement, University of Göttingen, Göttingen, Germany,* **1997**.
5. Farrugia, J. L. WinGx suite for small-molecule single crystal crystallography. *J. Appl. Crystallogr.***1999**, *32*, 837.
6. Bourhis, L.J.;Dolomanov, O.V.;Gildea, R.J.; Howard, J.A.K.;Puschmann, H. *ActaCryst.***2015**, *A71*, 59.
7. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J; Howard, J.A.K; Puschmann, H. *J. Appl. Cryst.***2009**, *42*, 339.