Electrochemical and Spectroelectrochemical Studies on Oxygen Reduction Mediated by Cu(II) Complexes Containing the Alkylamine Ligand N,N-Dimethylethylendiamine

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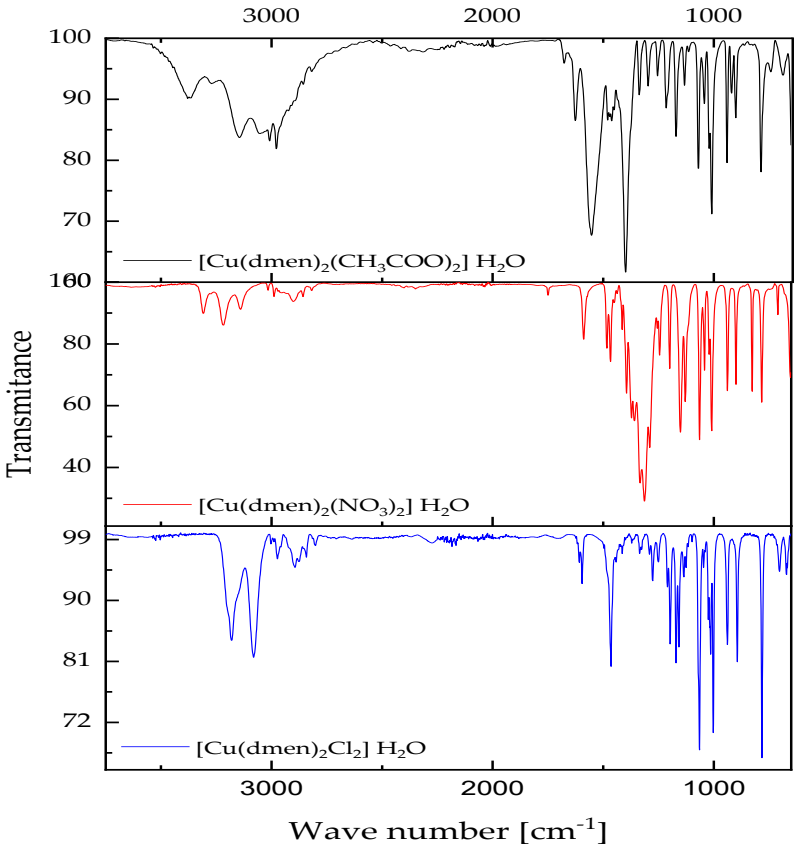

Figure S1.- IR spectra in ATR mode of [Cu(**dmen**)$_2$(CH$_3$COO)$_2$] H$_2$O, [Cu(**dmen**)$_2$(NO$_3$)$_2$] H$_2$O and [Cu(**dmen**)$_2$Cl$_2$] H$_2$O complexes.

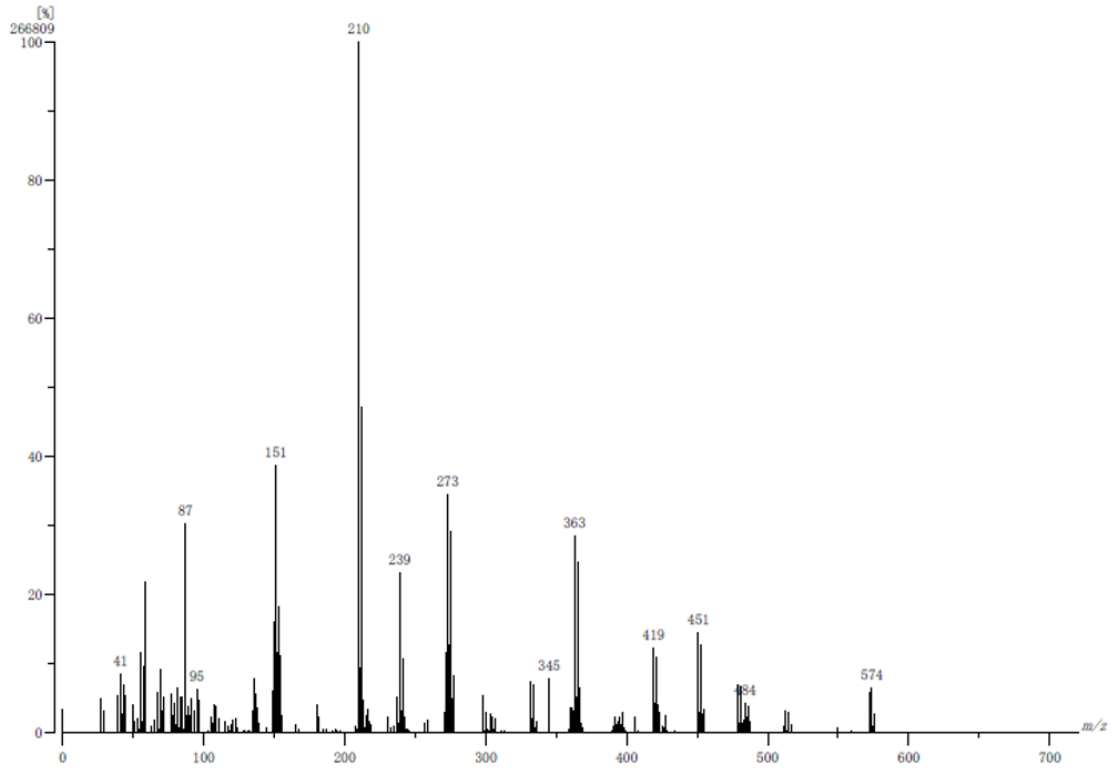

Figure S2.- Mass spectra of the complex [Cu(**dmen**)$_2$(CH_3COO)$_2$] H_2O.

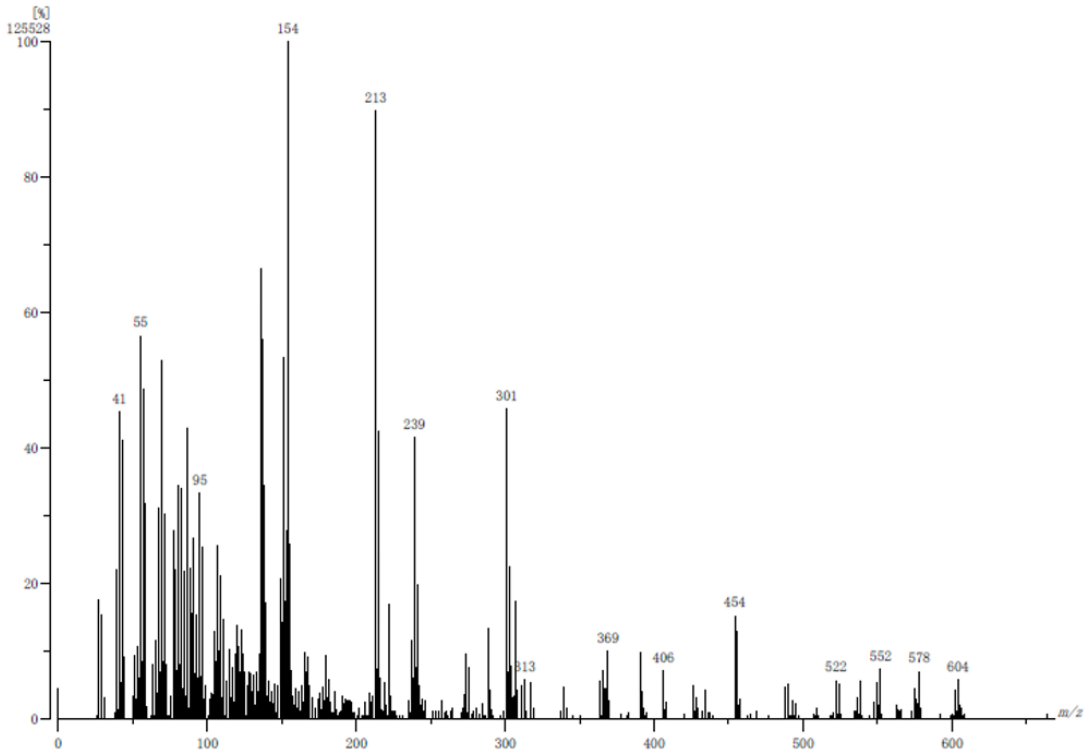

Figure S3.- Mass spectra of the complex [Cu(**dmen**)$_2$(NO_3)$_2$].

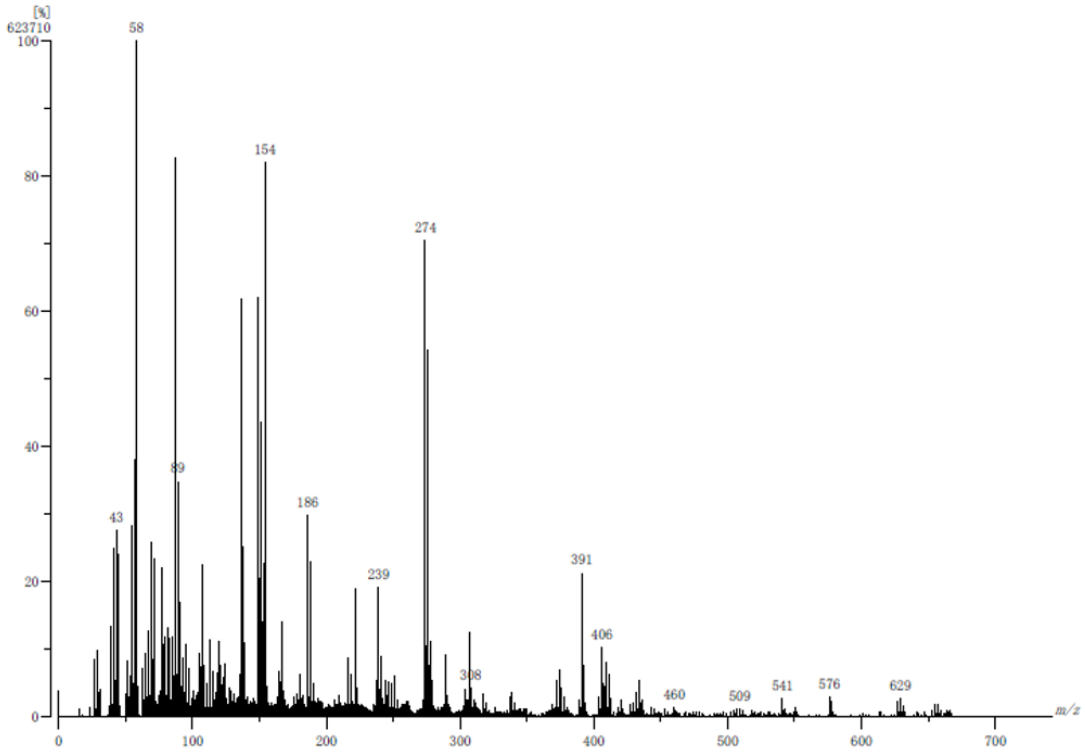

Figure S4.- Mass spectra of the complex $[Cu(dmen)_2Cl_2]$.

Table S1. Crystal and structure refinement data of $[Cu(dmen)_2(NO_3)_2]$ complex

Empirical formula	$C_8H_{24}CuN_6O_6$
Formula weight	36.87
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	C2/c
a/Å	10.1079(3)
b/Å	15.0349(4)
c/Å	9.9330(3)
α/°	90
β/°	97.989(3)
γ/°	90

Volume/Å^3	1494.88(8)
Z	4
ϱ_{calc}g/cm^3	1.617
μ/mm^{-1}	1.498
F(000)	764.0
Crystal size/mm^3	0.521 x 0.319 x 0.253
Radiation	Mo Kα (λ= 0.71073)
2Θ range for data collection/°	4.888 to 70.45
Index ranges	-16≤h≤16, -23≤k≤23, -16≤1≤15
Reflections collected	25000
Independent reflections	3233 [R_{int}= 0.0769, R_{sigma}= 0.0481]
Data/restraints/parameters	3233/0/100
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1= 0.0376, wR_2= 0.0837
Final R indexes [all data]	R_1= 0.0706, wR_2= 0.0947
Largest diff. peak/hole / e Å^{-3}	0.36/-0.33

Table S2. Selected Bond Lengths (Å) and Angles (deg) for [Cu(dmen)$_2$(NO$_3$)$_2$]

Atoms	Bond Length
Cu01-N02^1	2.0847(12)
Cu01-N02	2.0847(12)
Cu01-N01^1	1.9879(12)
Cu01-N01	1.9878(12)
Atoms	Angle
N02-Cu01-N02^1	180.0
N01^1-Cu01-N2	95.11(5)
N01-Cu01-N02	84.89(5)
N01^1-Cu01-N02^1	84.89(5)

N01-Cu01-N02[1]	95.11(5)
N01[1]-Cu01-N01	180.0

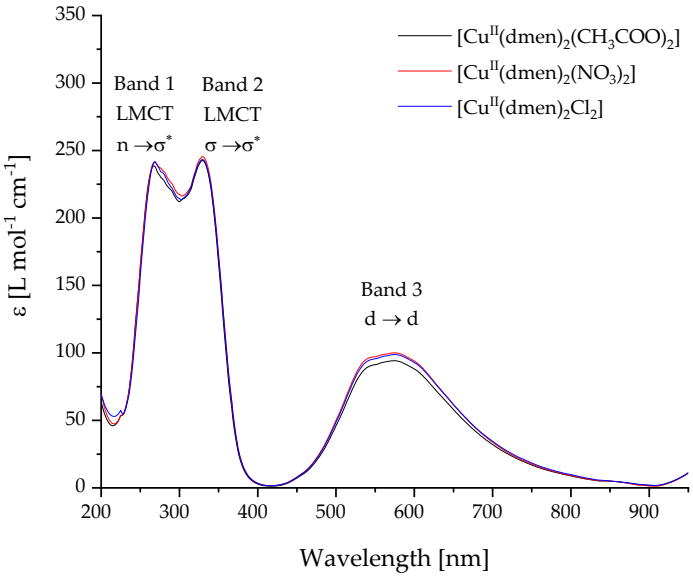

Figure S5. Electronic spectra of mononuclear Cu(II) complexes in aqueous solution + KNO_3 0.1 M

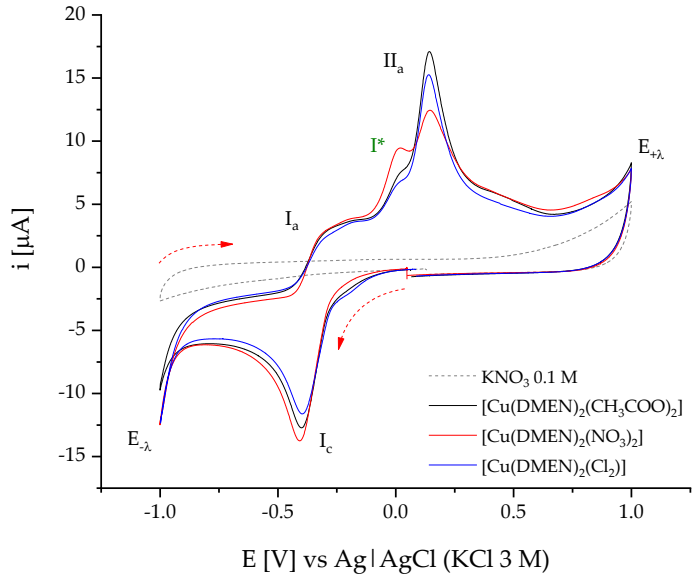

Figure S6.- Cyclic voltammograms of $1x10^{-3}$ M solution of mononuclear Cu(II) complexes in negative direction at scan rate 0.1 V seg^{-1}. Electrolyte= H_2O + KNO_3 0.1 M, E_w= glassy carbon.

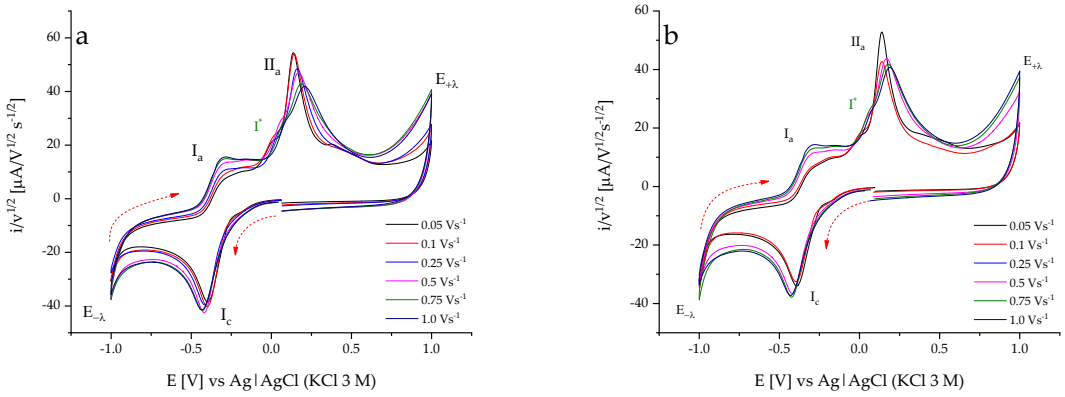

Figure S7.- Cyclic voltammograms of 1x10^{-3} M solution in normalizes current representation (i/$\nu^{1/2}$) of complexes a) [Cu(**dmen**)$_2$(CH$_3$COO)$_2$] H$_2$O, b) [Cu(**dmen**)$_2$(Cl$_2$)] H$_2$O in negative direction at scan rate from 0.1 to 1 V seg^{-1}. Electrolyte= H$_2$O + KNO$_3$ 0.1 M; E$_W$= glassy carbon.

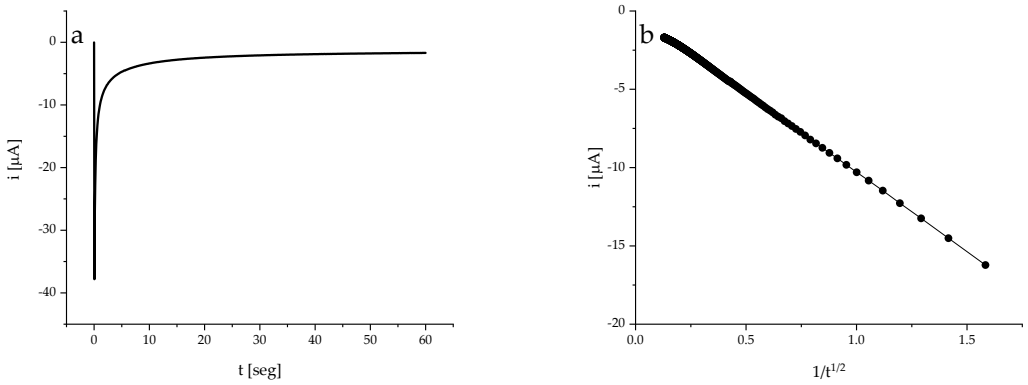

Figure S8.- One step Chronoamperometry of 1x10^{-3} M solution of [Cu(dmen)$_2$(NO$_3$)$_2$] a) I vs t and plot b) i vs t$^{-1/2}$ plot. Electrolyte= H$_2$O + KNO$_3$ 0.1 M; E$_W$= glassy carbon, Ei= -0.5 V vs Ag|AgCl, τ= 60 seconds.

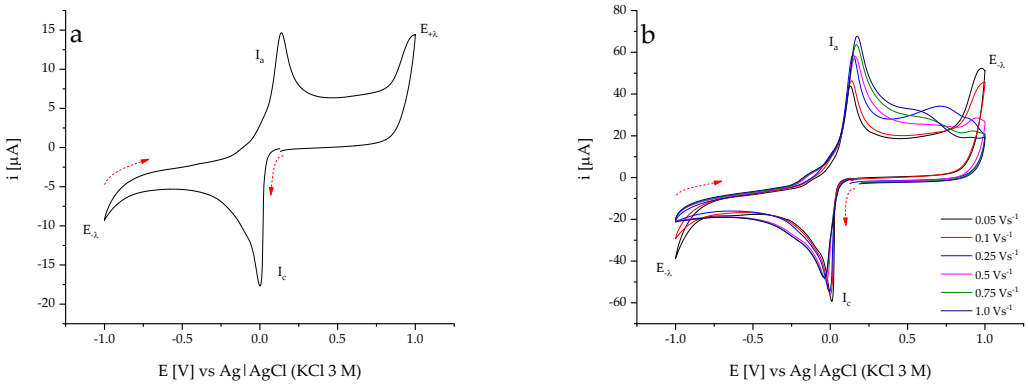

Figure S9.- Cyclic voltammetry of 1x10^{-3} M solution of complex [Cu(1,10-phen)$_2$NO$_3$]NO$_3$ in

negative direction at a) scan rate of 0.1 V seg^{-1} and b) normalized representation ($i/v^{1/2}$) at scan rate from 0.1 to 1 V seg^{-1}. Electrolyte= H_2O + KNO_3 0.1 M; E_W= glassy carbon.

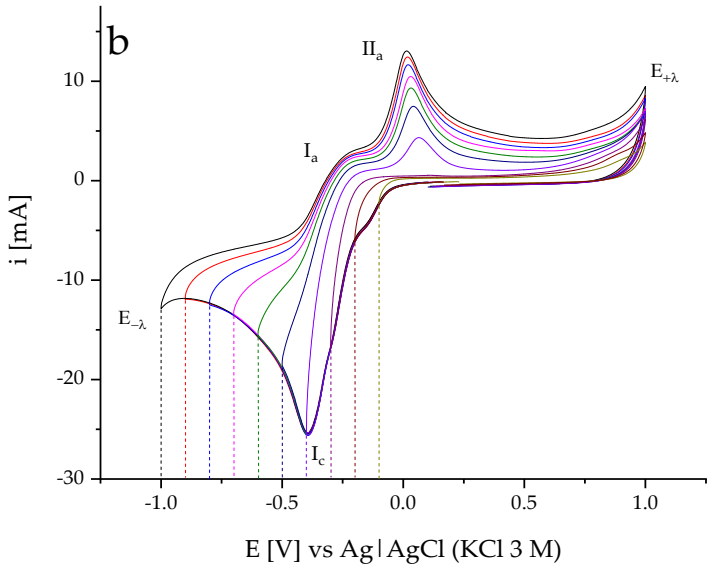

Figure S10.- Inversion potential analysis of 1x10^{-3} M solution of complex [Cu(dmen)$_2$(NO_3)$_2$] in negative direction at scan rate 0.1 V seg^{-1} in the presence of O_2. Electrolyte= H_2O + KNO_3 0.1 M; E_W= glassy carbon.

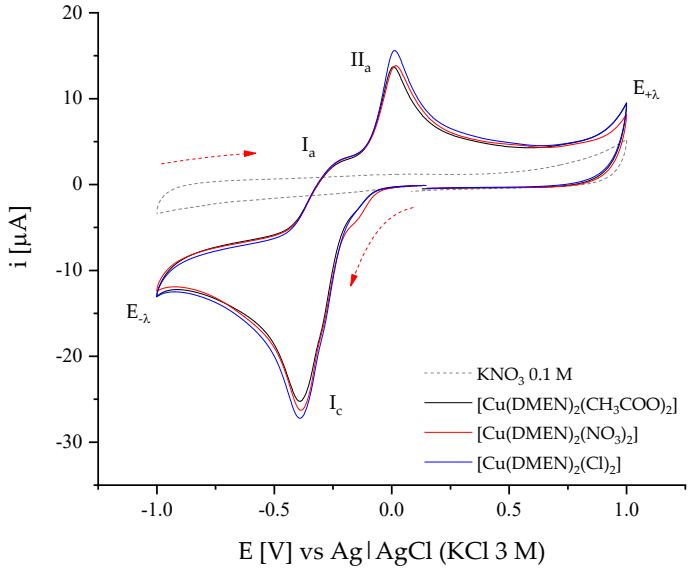

Figure S11.- Cyclic voltammograms of 1x10^{-3} M solution of complexes [Cu(dmen)$_2$(CH_3COO)$_2$] H_2O, [Cu(dmen)$_2$(NO_3)$_2$] H_2O and [Cu(dmen)$_2Cl_2$] H_2O in presence of O_2 in negative direction at scan rate 0.1 V seg^{-1}. Electrolyte= H_2O + KNO_3 0.1 M; E_W= glassy carbon.

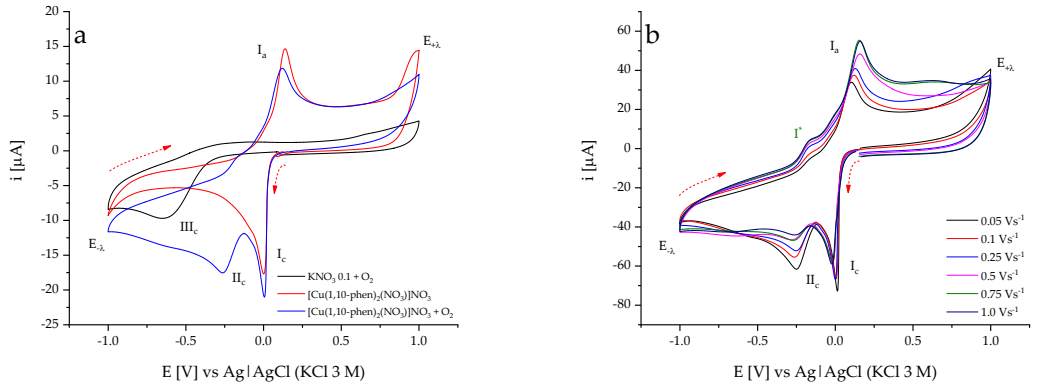

Figure S12.- Cyclic voltammograms of 1x10^{-3} M solution of complex [Cu(1,10-phen)$_2$NO$_3$]NO$_3$ + O$_2$ in negative direction at a) scan rate 0.1 V seg^{-1} and b) normalized representation (i/v$^{1/2}$) at scan rate from 0.1 to 1 V seg^{-1}. Electrolyte= H$_2$O + KNO$_3$ 0.1 M; E$_W$= glassy carbon.

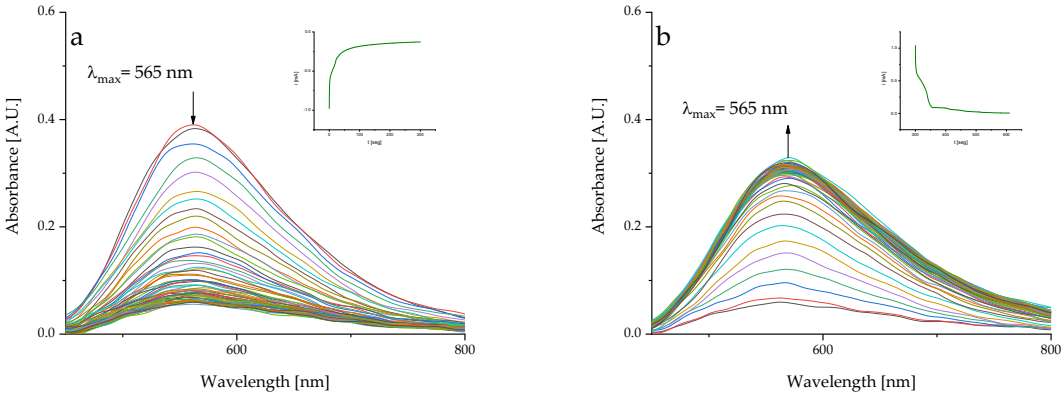

Figure S13. UV-Vis spectroelectrochemical response of 1.5x10^{-2} M solution of complex [Cu(dmen)$_2$(NO$_3$)$_2$], a) E$_1$= -0.85 V vs Ag|AgCl, inset chronoamperometric plot, and b) E$_2$= 0.25 V vs Ag|AgCl, inset chronoamperometric plot. Electrolyte= H$_2$O + KNO$_3$ 0.1 M; E$_W$= commercial Pt honeycomb, spectra acquired each 5 seg for 10 minutes.

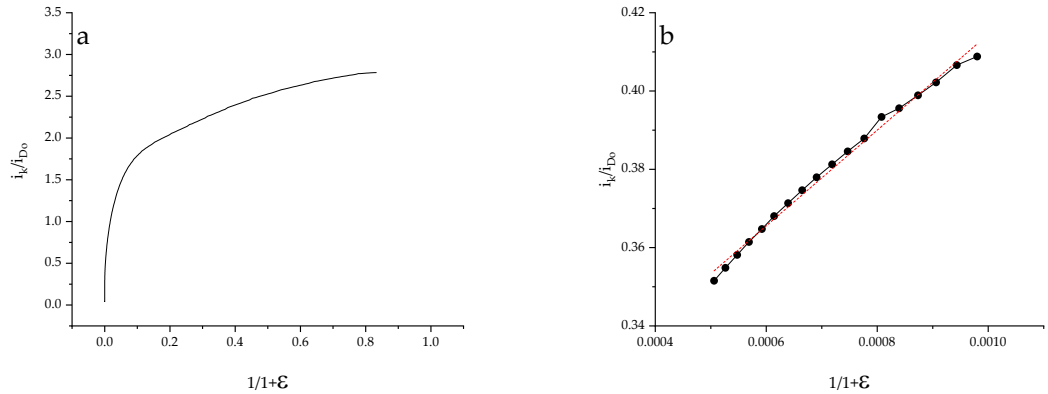

Figure S14.- ORR FOWA plot of 1x10^{-3} M solution of complex [Cu(DMEN)$_2$(CH$_3$COO)$_2$] a) adjusted plot to eq (4) and b) linearly adjusted plot to -0.142 - -0.159 V potentials. Cyclic voltammetry performed in negative direction, electrolyte= H_2O + KNO_3 0.1 M, E_w= glassy carbon, ν= 0.1 V seg^{-1}.

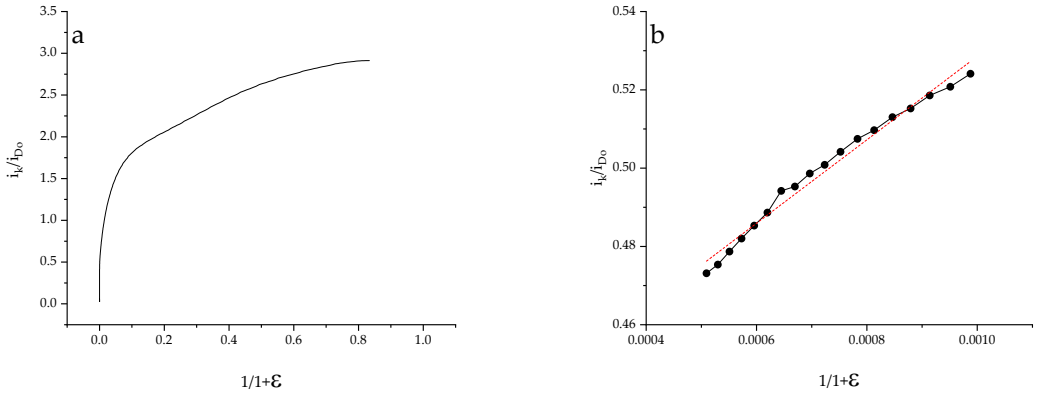

Figure S15.- ORR FOWA plot of 1x10^{-3} M solution of complex [Cu(DMEN)$_2$(NO$_3$)$_2$] a) adjusted plot to eq (4) and b) linearly adjusted plot to -0.142 - -0.159 V potentials. Cyclic voltammetry performed in negative direction, electrolyte= H_2O + KNO_3 0.1 M, E_w= glassy carbon, ν= 0.1 V seg^{-1}.

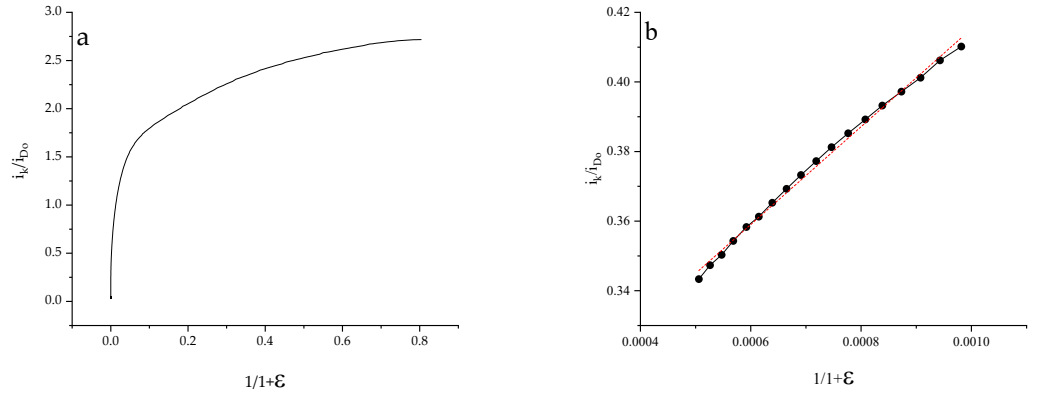

Figure S16. ORR FOWA plot of 1x10^{-3} M solution of complex [Cu(DMEN)$_2$(Cl$_2$)] a) adjusted plot to eq (4) and b) linearly adjusted plot to -0.142 - -0.159 V potentials. Cyclic voltammetry performed in negative direction, electrolyte= H_2O + KNO_3 0.1 M, E_w= glassy carbon, ν= 0.1 V seg^{-1}.

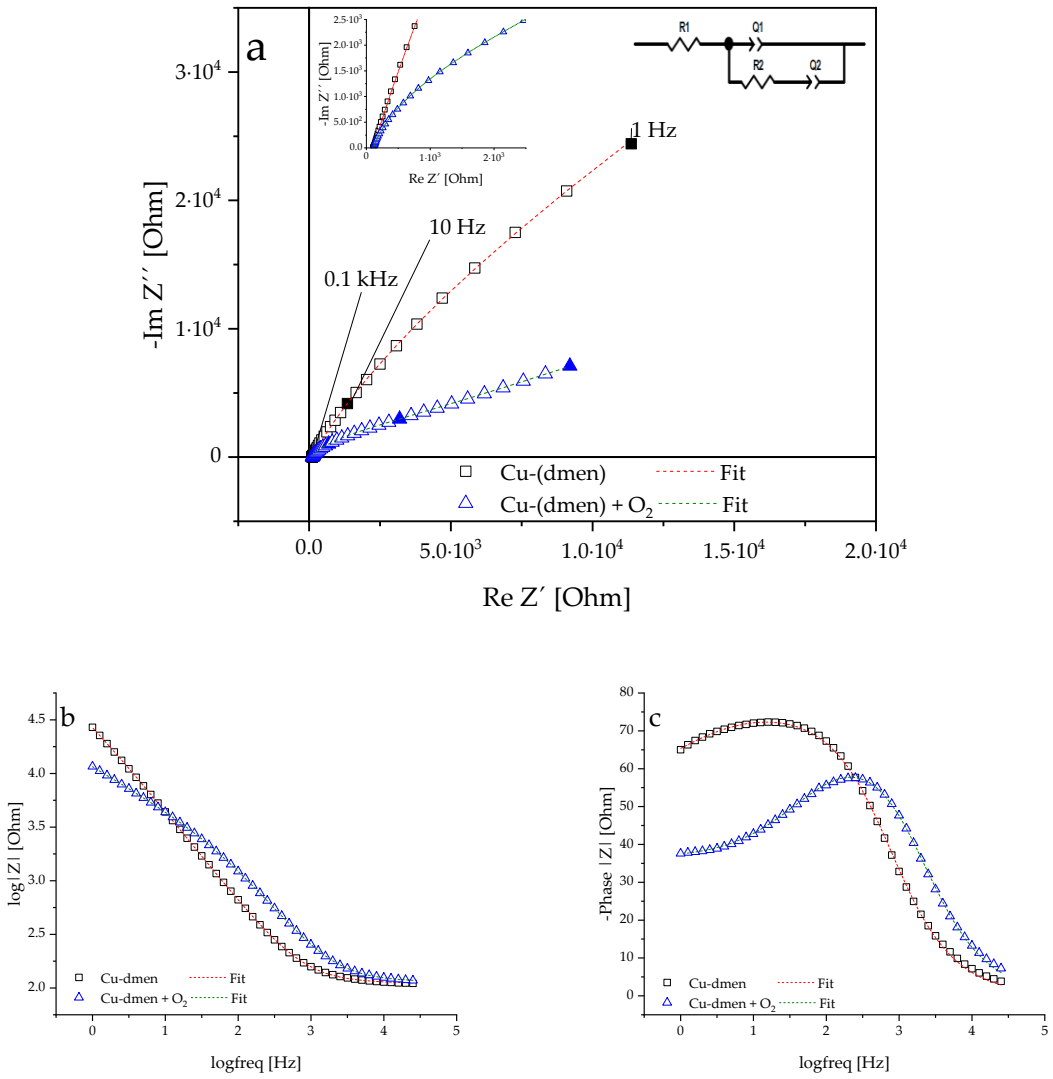

Figure S17. EIS spectrums of 1x10^{-3} M solution of complex [Cu(DMEN)$_2$(CH$_3$COO)$_2$] in absence and presence of O$_2$; a) Nyquist, b) Bode-module and c) Bode-phase diagrams. Electrolyte= H$_2$O + KNO$_3$ 0.1 M, E$_w$: glassy carbon, E$_{DC}$: -0.55 V, E$_{AC}$: 10 mV, , n$_d$: 10, 100 kHz – 1 Hz.

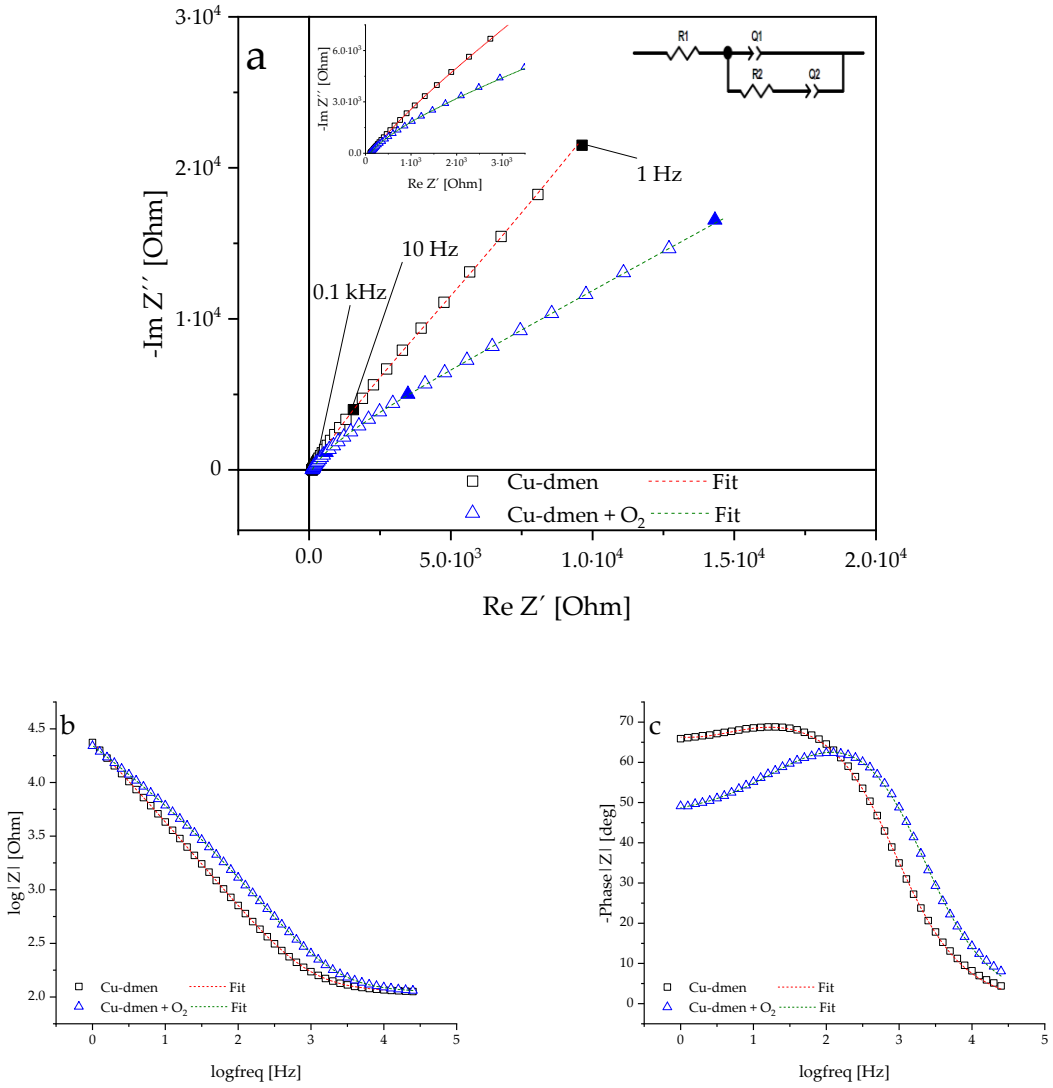

Figure S18. EIS spectrums of 1x10^{-3} M solution of complex [Cu(DMEN)$_2$Cl$_2$] in absence and presence of O$_2$; a) Nyquist, b) Bode-module and c) Bode-phase diagrams. Electrolyte= H$_2$O + KNO$_3$ 0.1 M, E$_w$: glassy carbon, E$_{DC}$: -0.5 V, E$_{AC}$: 10 mV, , n$_d$: 10, 100 kHz – 1 Hz.

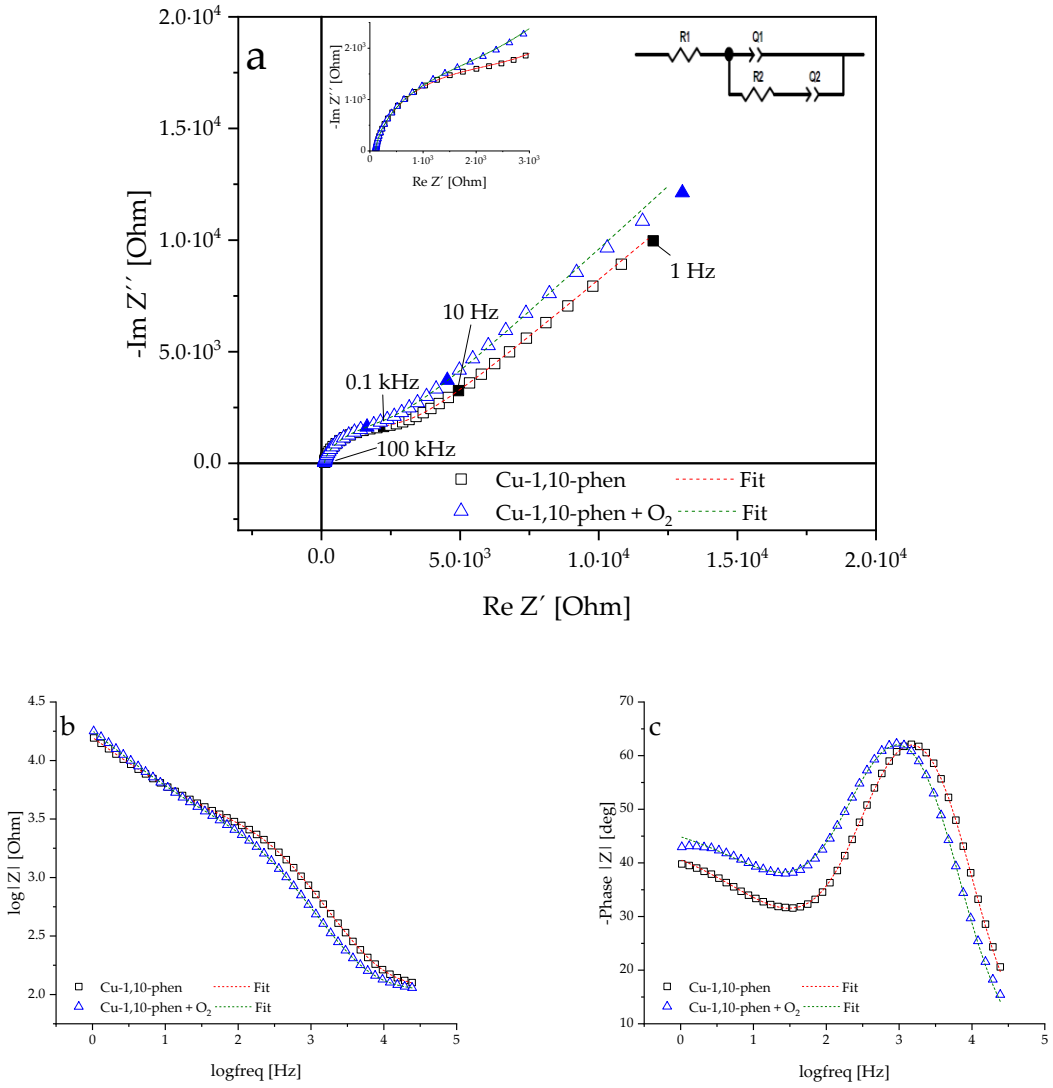

Figure S19. EIS spectrums of 1x10^{-3} M solution of complex [Cu(1,10-phen)$_2$(NO$_3$)]NO$_3$ in absence and presence of O$_2$; a) Nyquist, b) Bode-module and c) Bode-phase diagrams. Electrolyte= H$_2$O + KNO$_3$ 0.1 M, E$_w$: glassy carbon, E$_{DC}$: -0.05 V, E$_{AC}$: 10 mV, , n$_d$: 10, 100 kHz – 1 Hz.

Table S3. Fitted parameter of Cu(II) mononuclear complexes; electrolyte: H_2O + KNO_3 0.1 M, E_w: glassy carbon, E_{DC}: -0.5 V vs Ag|AgCl, E_{AC}: 10 mV, n_d: 10, 100 kHz – 1 Hz.

Complex		R_1 [Ohm]	Q_1 [μF]	a_1	R_2 [Ohm]	Q_2 [μF]	a_2	χ^2
1	without O_2	110.3	6.6218	0.85039	57190	6.5392	0.46954	6.9438E-05
	with O_2	114.1	2.8423	0.85291	2180	41.735	0.41468	2.5255E-05
2	without O_2	123.8	1.6168	0.8838	36391	2.1634	0.48765	5.8883E-05
	with O_2	121.7	1.3016	0.88222	5543	23.582	0.42582	3.5177E-05
3	without O_2	110.7	7.7929	0.81467	52491	3.4736	0.70583	2.7697E-05
	with O_2	110	3.622	0.82489	6134	15.106	0.48253	3.6733E-05
Cu(1,10-phen)	without O_2	112.9	0.34875	0.9302	2513	27.469	0.51246	1.5086E-05
	with O_2	106.6	0.55874	0.92606	2388	21.781	0.53971	5.5934E-05