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Electronic Supplementary Information

Unusual Chemistry of Cu(II) Salan Complexes: Synthesis, Characterization and Superoxide Dismutase Activity

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Electronic spectral data for complexes

Table S1 Electronic spectral data for complexes **1**-**4** in DMSO.

Complexes	λ_{max}/nm (ε/M^{-1} cm^{-1})
1	296 (15109), 352 (2121), 424 (2445), 609 (657)
2	286 (23121), 344 (2023), 424 (2788), 613 (589)
3	295 (20338), 397 (1555), 429 (2223), 605 (770)
4	294 (11384), 371 (1563), 419 (2312), 601 (431)

Supplementary single crystal X-ray diffraction data.

Table S2(a) Selected bond parameters in H_2L^3.

Bond lengths (Å)			
O(1)-C(10)	1.367(2)	N(1)-C(4)	1.485(3)
O(2)-C(21)	1.367(2)	N(1)-C(3)	1.461(2)
N(2)-C(25)	1.468(3)	N(2)-C(3)	1.465(2)
Bond angles (°)			
N(1)-C(3)-N(2)	104.44(15)	N(2)-Cu(1)-O(2)	92.2(2)

Table S2(b) Intramolecular hydrogen bonds in compound H_2L^3**.**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...N(1)	0.84(3)	1.83(3)	2.615(2)	155(3)
O(2)-H(2O)...N(2)	0.90(3)	1.80(3)	2.628(2)	153(3)

Table S3 Selected geometric parameters (Å, °) for the Cu-complexes **1A**, **3** and **4**

[Cu(L^1)(DMSO)] (**1A**)			
Bond lengths (Å)			
N(1)-Cu(1)	2.054(7)	N(2)-Cu(1)	2.047(5)
O(1)-Cu(1)	1.863(5)	O(2)-Cu(1)	1.901(5)
O(3)-Cu(1)	2.41(1)		
Bond angles (°)			
N(1)-Cu(1)-N(2)	86.0(3)	N(2)-Cu(1)-O(2)	92.2(2)
N(1)-Cu(1)-O(1)	91.3(2)	N(2)-Cu(1)-O(3)	89.7(3)
N(1)-Cu(1)-O(2)	162.8(2)	O(1)-Cu(1)-O(2)	88.2(2)
N(1)-Cu(1)-O(3)	97.3(3)	O(1)-Cu(1)-O(3)	98.1(3)
N(2)-Cu(1)-O(1)	172.0(2)	O(2)-Cu(1)-O(3)	99.8(3)
N(1)-Cu(1)-N(2)	86.0(3)	N(2)-Cu(1)-O(2)	92.2(2)
[Cu(L^{3A})]$_2$ (**3**)			
Bond lengths (Å)			
O(1)-Cu(1)	1.971(8)	N(1)-Cu(1)	1.968(10)
O(2)-Cu(1)	1.909(8)	N(2)-Cu(1)	2.042(9)
O(1^i)-Cu(1)	2.786(10)	O(3)-Cu(1)	2.544(9)
Cu(1)-Cu(1^i)	3.732(4)	Cu(2)-Cu(2^i)	3.381(3)
Bond angles (°)			
O(2)-Cu(1)-N(1)	151.5(4)	O(2)-Cu(1)-O(1)	100.2(3)
N(1)-Cu(1)-O(1)	91.3(4)	O(2)-Cu(1)-N(2)	91.9(4)
N(1)-Cu(1)-N(2)	86.2(4)	O(1)-Cu(1)-N(2)	158.7(4)
[Cu(L^{4A})] (**4**)			
Bond lengths (Å)			
N(2)-Cu(1)	2.002(2)	O(2)-Cu(1)	1.896(3)
N(1)-Cu(1)	2.052(3)	O(1)-Cu(1)	1.878(2)
Bond angles (°)			
N(2)-Cu(1)-N(1)	85.8(1)	N(1)-Cu(1)-O(2)	173.4(1)
N(2)-Cu(1)-O(2)	92.9(1)	N(1)-Cu(1)-O(1)	93.2(1)
N(2)-Cu(1)-O(1)	170.2(1)	O(2)-Cu(1)-O(1)	89.1(1)

^{1}H and ^{13}C NMR spectra of ligand precursor

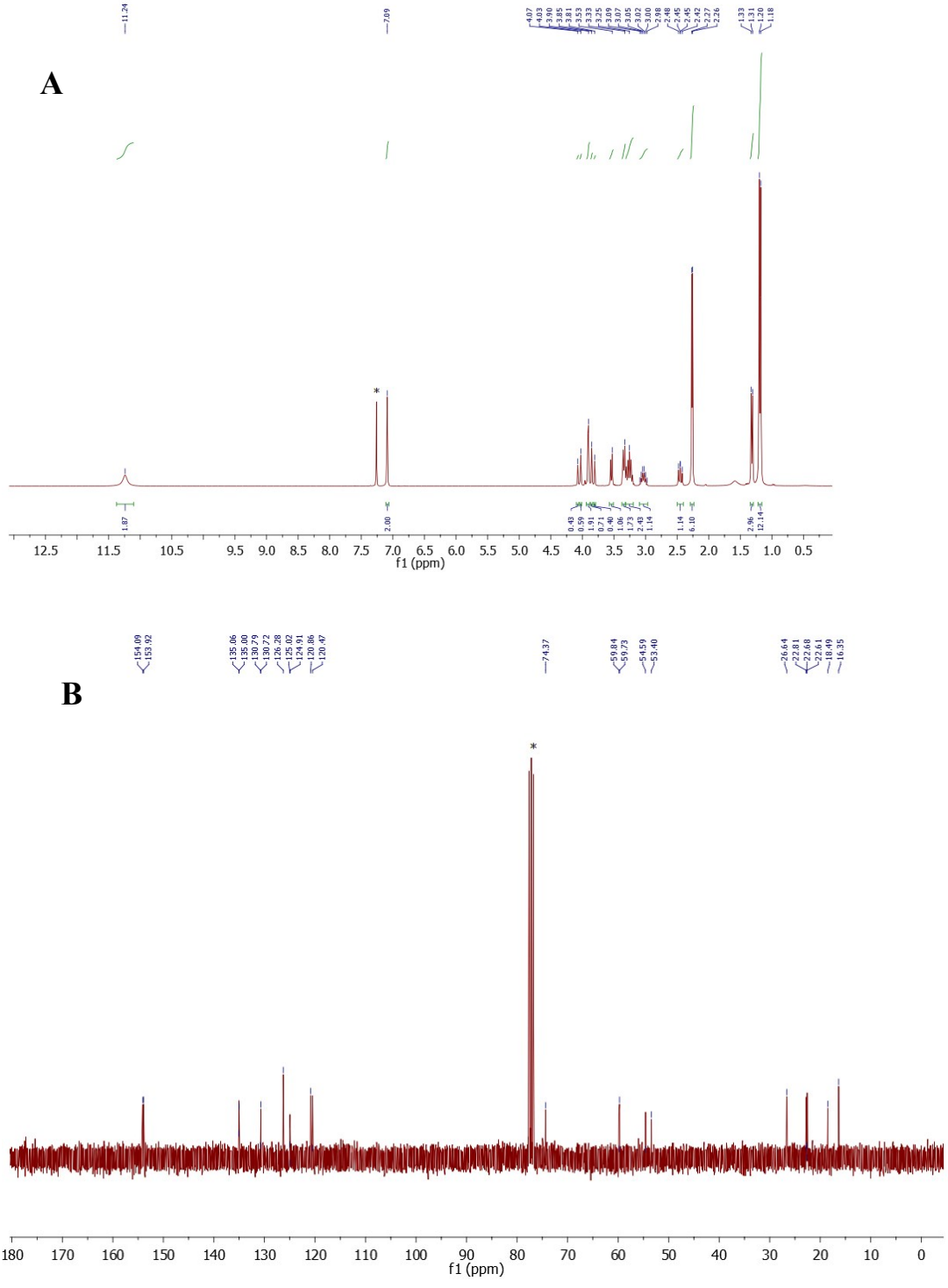


Fig. S1 ^{1}H NMR (A) and ^{13}C NMR (B) spectrum of H_2L^3 in $CDCl_3$ (* marks the solvent signal).

ESI-MS spectra

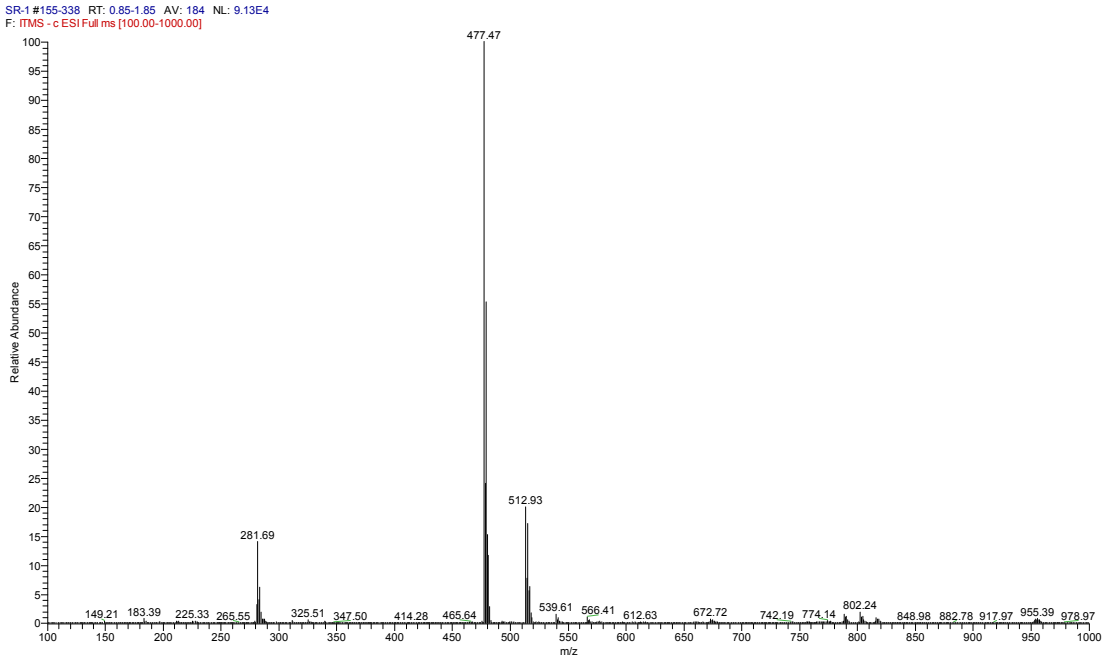


Fig. S2(a) ESI-MS spectrum of H_2L^3 in the negative ion mode (MeOH solution).

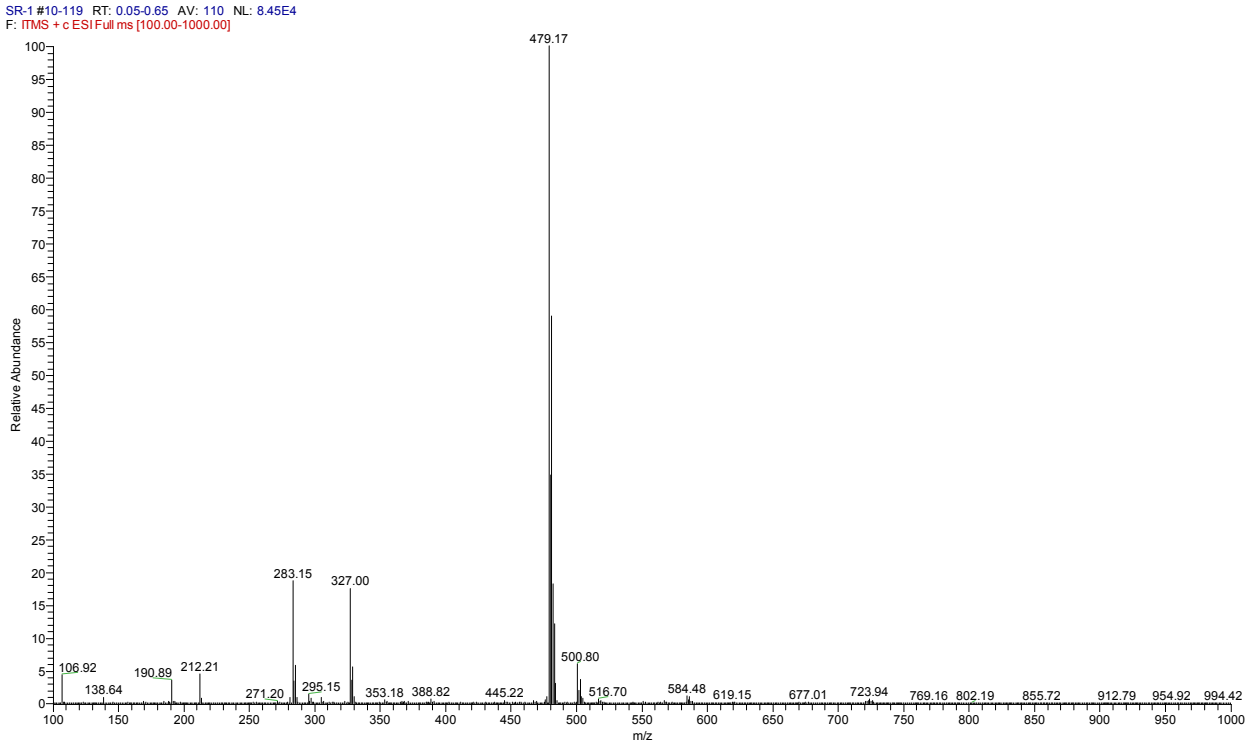


Fig. S2(b) ESI-MS spectrum of H_2L^3 in the positive ion mode (MeOH solution).

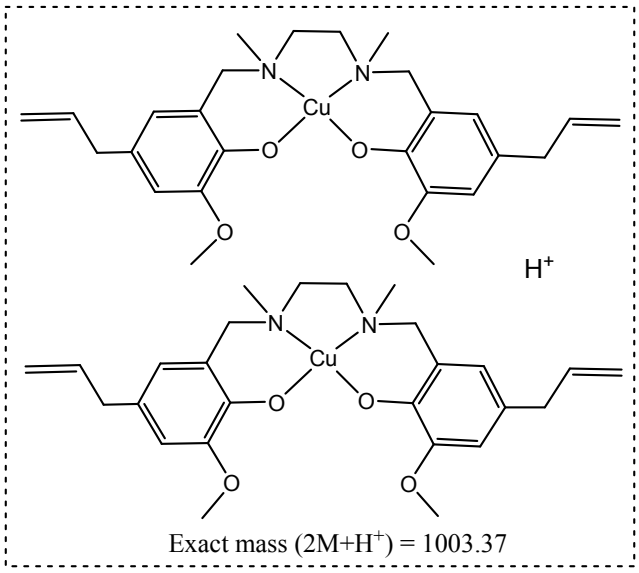


Fig. S3 Proposed molecular formulae for species found in the ESI-MS spectrum of **2**.

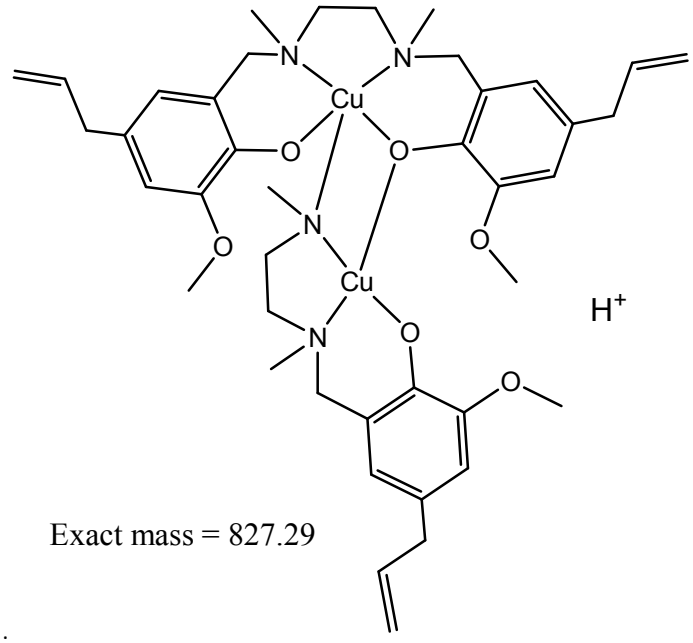


Fig. S4 Proposed molecular formulae for deaminated species found in the ESI-MS spectrum of **2**.

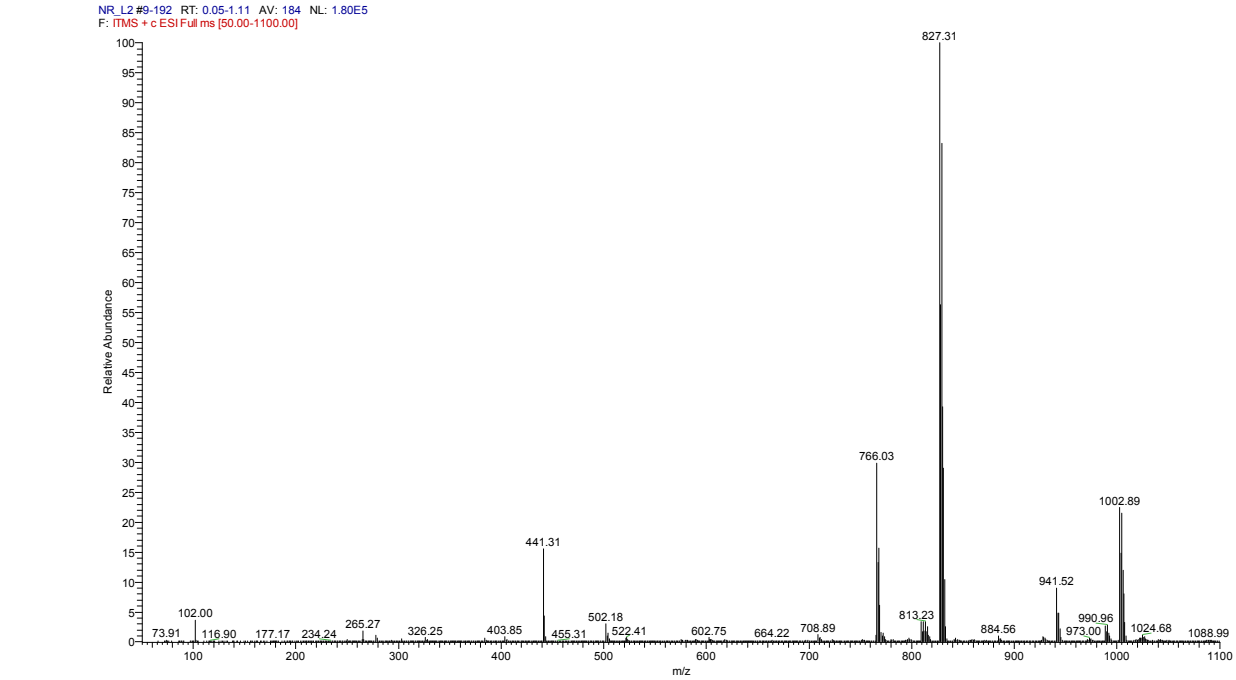


Fig. S5 ESI-MS spectrum of **2** in the positive ion mode (MeOH solution).

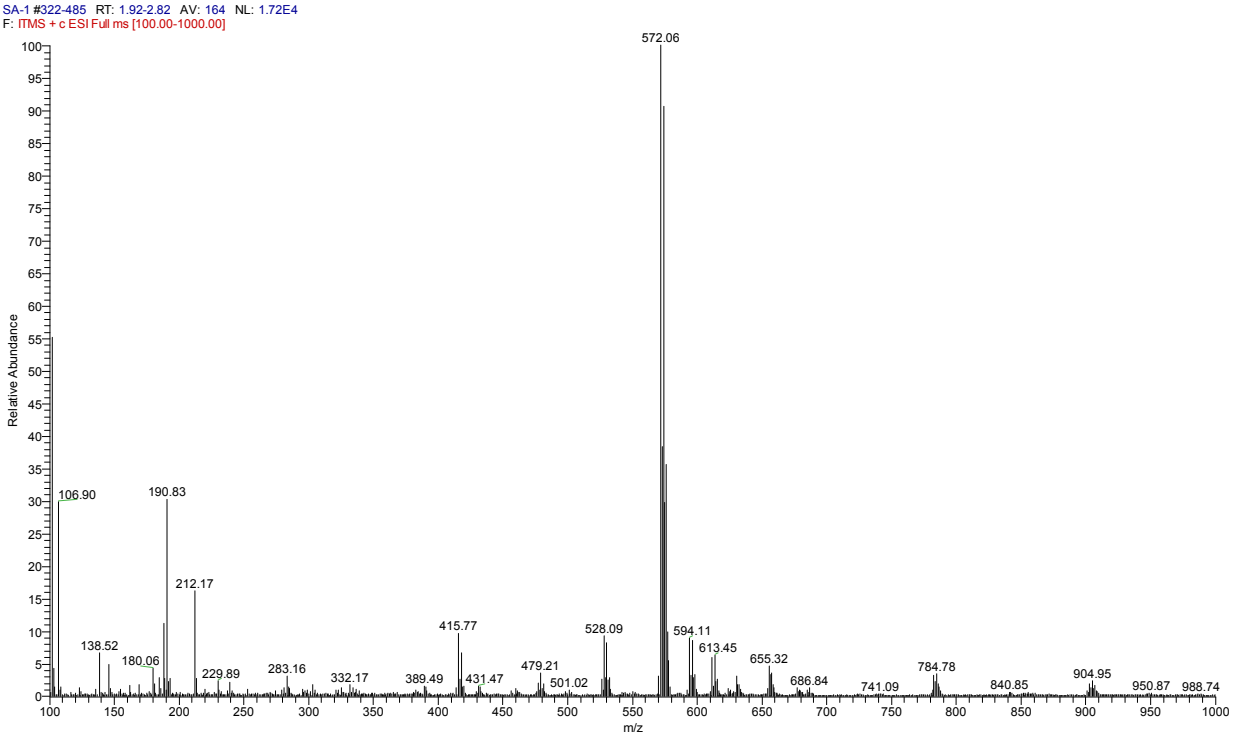


Fig. S6 ESI-MS spectrum of **3** in the positive ion mode (MeOH solution).

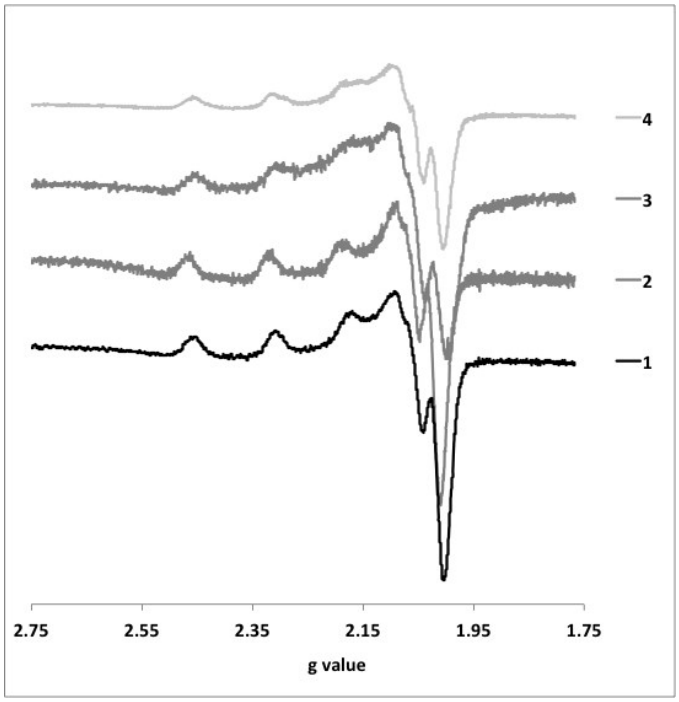


Fig. S7 First derivative EPR spectra of frozen solutions of the Cu-complexes **1**-**4** in DMF (*ca.* 3 mM), measured at ca. 100 K.

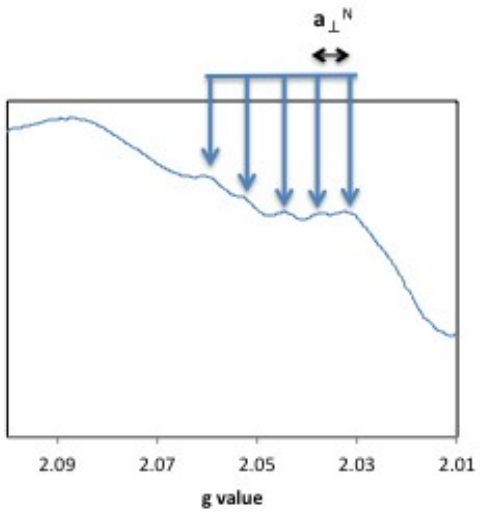
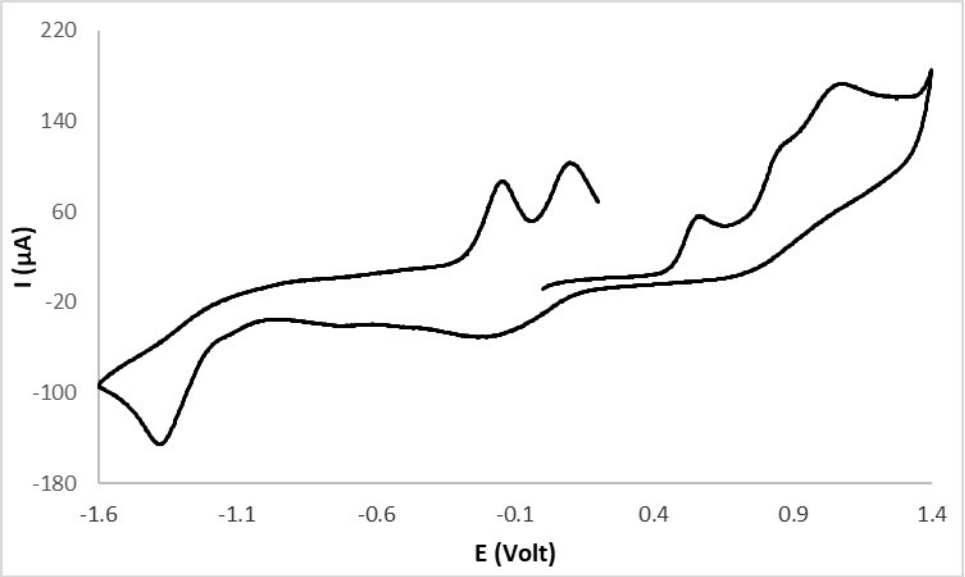


Fig S8 X-band EPR spectrum of **4** evidencing the superhyperfine structure in the perpendicular region resulting from spin-coupling of the unpaired electron with two ^{14}N nuclei.

Additional Electrochemical data

a)



b)

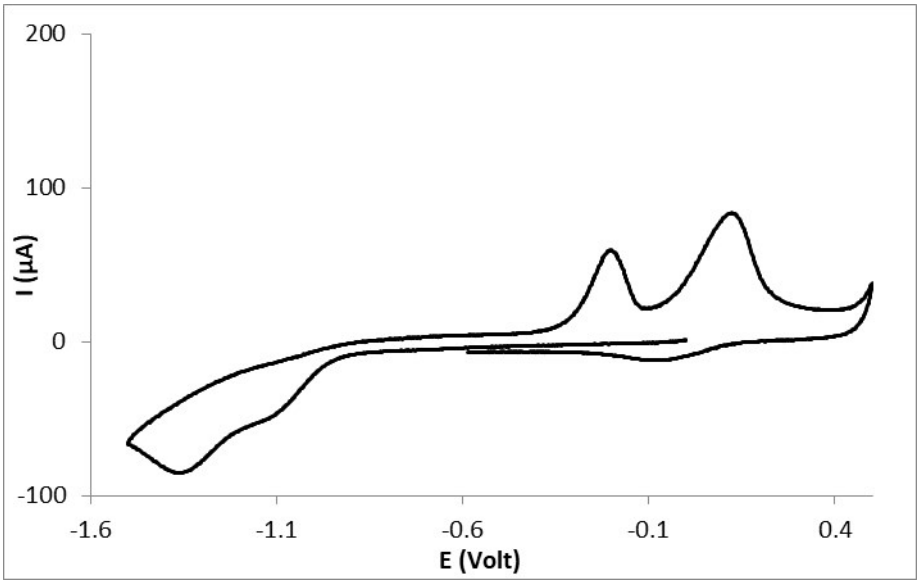
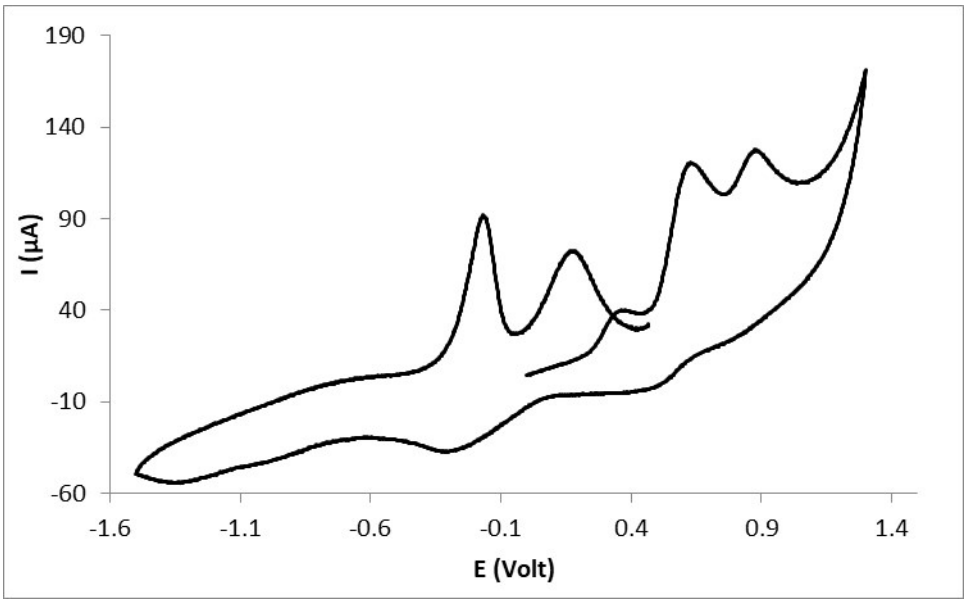


Fig. S9 Cyclic voltammogram of complex **1**. (a) anodic scan; (b) cathodic scan. The cyclic voltammograms were obtained in NBu_4BF_4/DMF (0.1 M) at 200 mV/s.

a)



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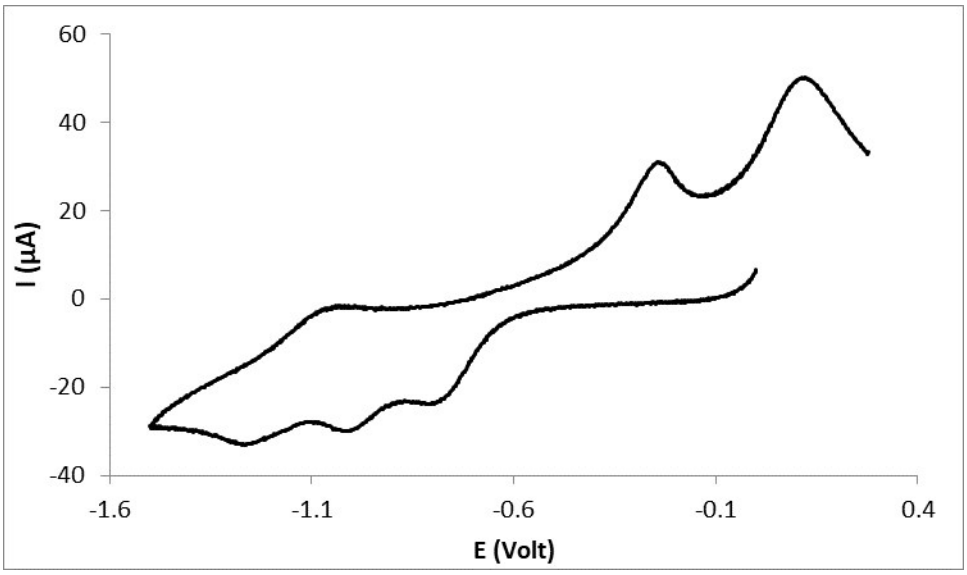
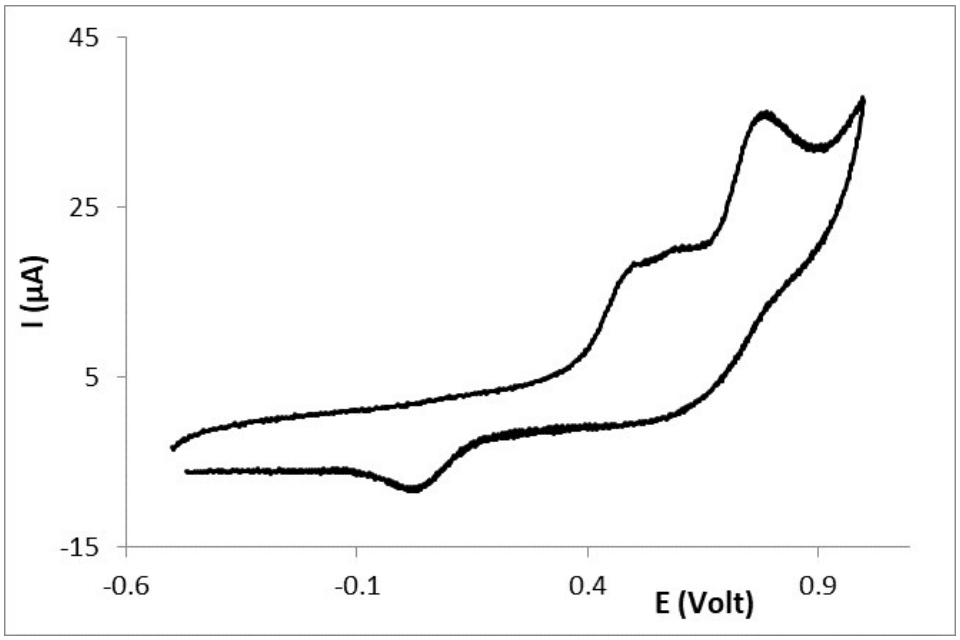


Fig. S10 Cyclic voltammogram of complex **2**. (a) anodic scan; (b) cathodic scan. The cyclic voltammograms were obtained in NBu_4BF_4/DMF (0.1M) at 200 mV/s.

a)



b)

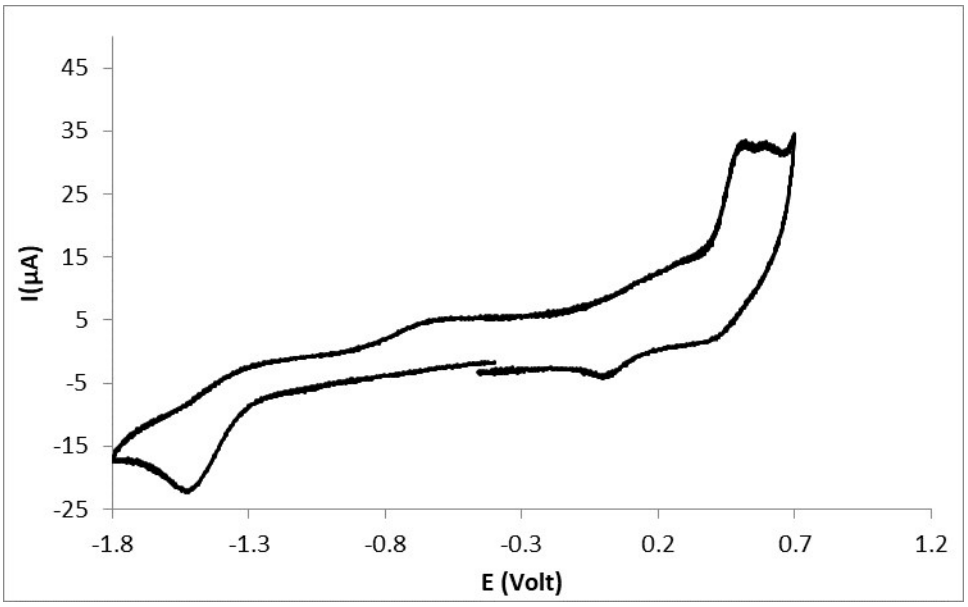
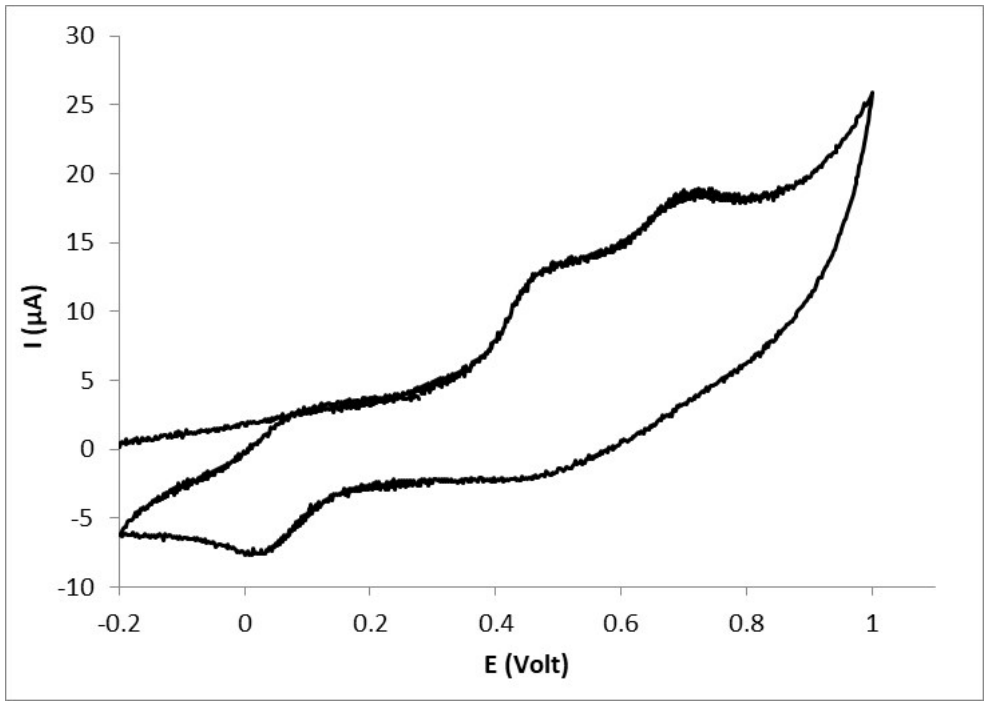


Fig. S11 Cyclic voltammogram of complex **3**. (a) anodic scan; (b) cathodic scan. The cyclic voltammograms were obtained in NBu_4BF_4/DMF (0.1M) at 200 mV/s.

a)



b)

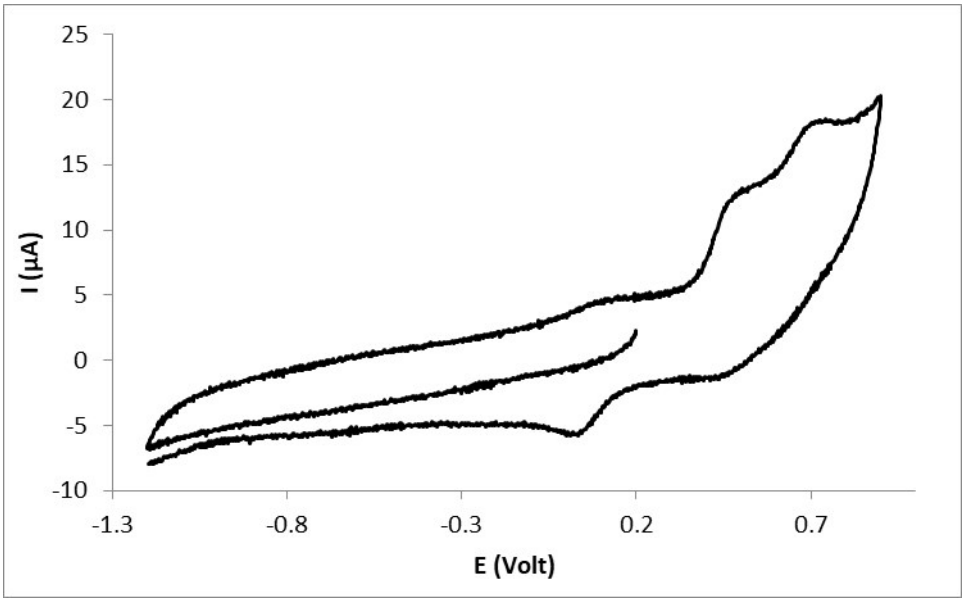


Fig. S12 Cyclic voltammogram of complex **4**. (a) anodic scan; (b) cathodic scan. The cyclic voltammograms were obtained in NBu_4BF_4/DMF (0.1M) at 200 mV/s.

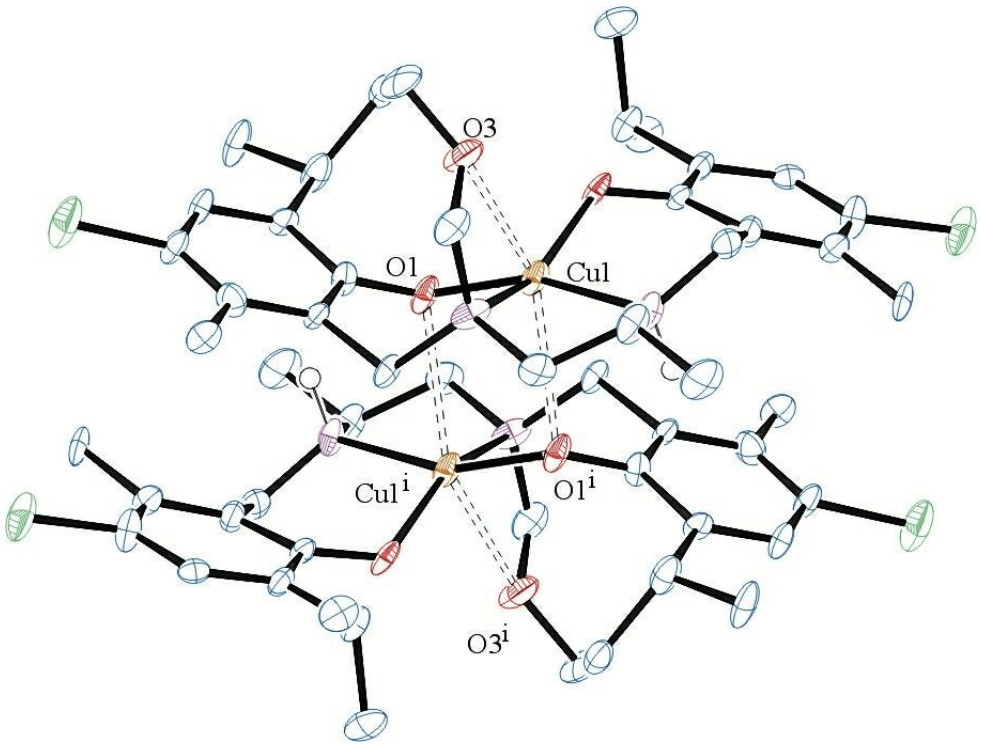


Fig. S13 ORTEP diagram of $[Cu(L^{3A})]_2$ (**3**) showing the weak interactions 50% probability level (Bond distance, Cu(1)-Cu(1^{i})= 3.732(4) Å)

Evaluation of Superoxide dismutase activity

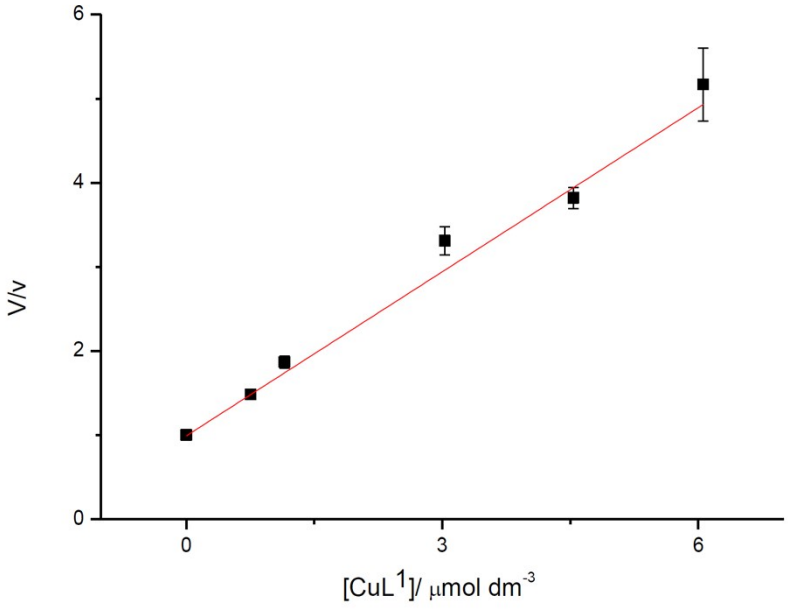


Fig. S14 Plot of V/v *vs.* complex concentration of [CuL[1]] (**1**) employed for IC_{50} calculation. V/v is the ratio between the NBT reduction rate in the absence (V) and in the presence (v) of different concentration of complex **1**. The IC_{50} is the value at V/v = 2.

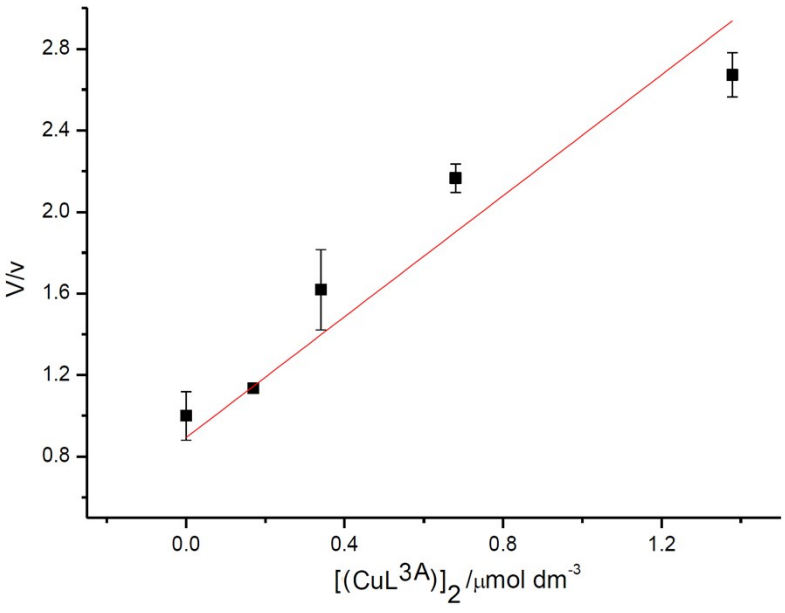


Fig. S15 Plot of V/v *vs.* complex concentration of $[(CuL^{3A})]_2$ (**3**) employed for IC_{50} calculation. V/v is the ratio between the NBT reduction rate in the absence (V) and in the presence (v) of different concentration of complex **3**. The IC_{50} is the value at V/v = 2.