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Electronic supplementary information

***C*$_i$-symmetry, [2 × 2] grid, square copper complex with the *N*^{4},*N*^{5}-bis(4-fluorophenyl)-1*H*-imidazole-4,5-dicarboxamide ligand. Structure, catecholase activity, magnetic properties and DFT calculations**

Arfa Parween, Sumita Naskar, Antonio J. Mota,* Arturo Espinosa Ferao, Shyamal Kumar Chattopadhyay Eric Riviere,* William Lewis, Subhendu Naskar*

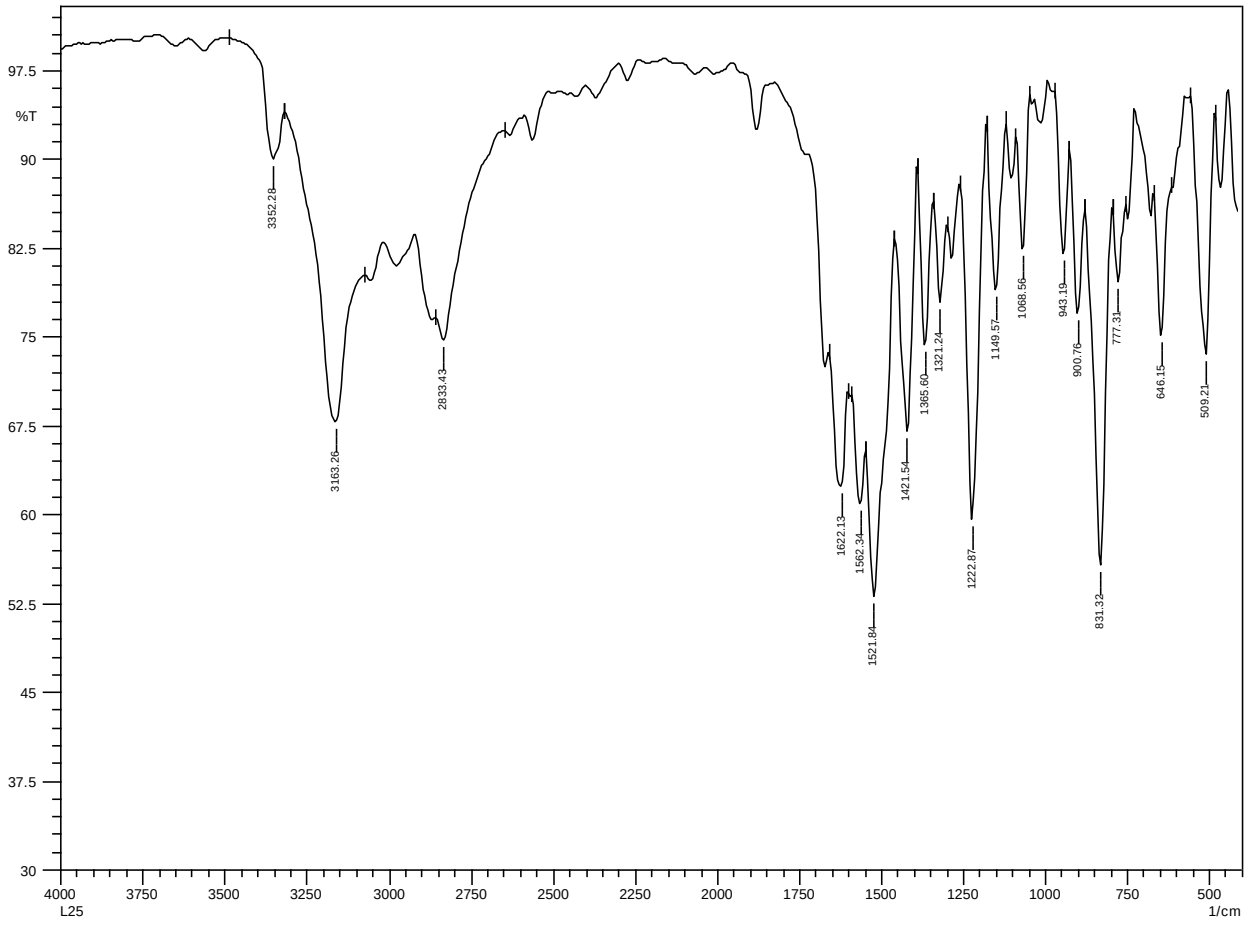

Figure S1: IR spectrum of the ligand **LH_3**.

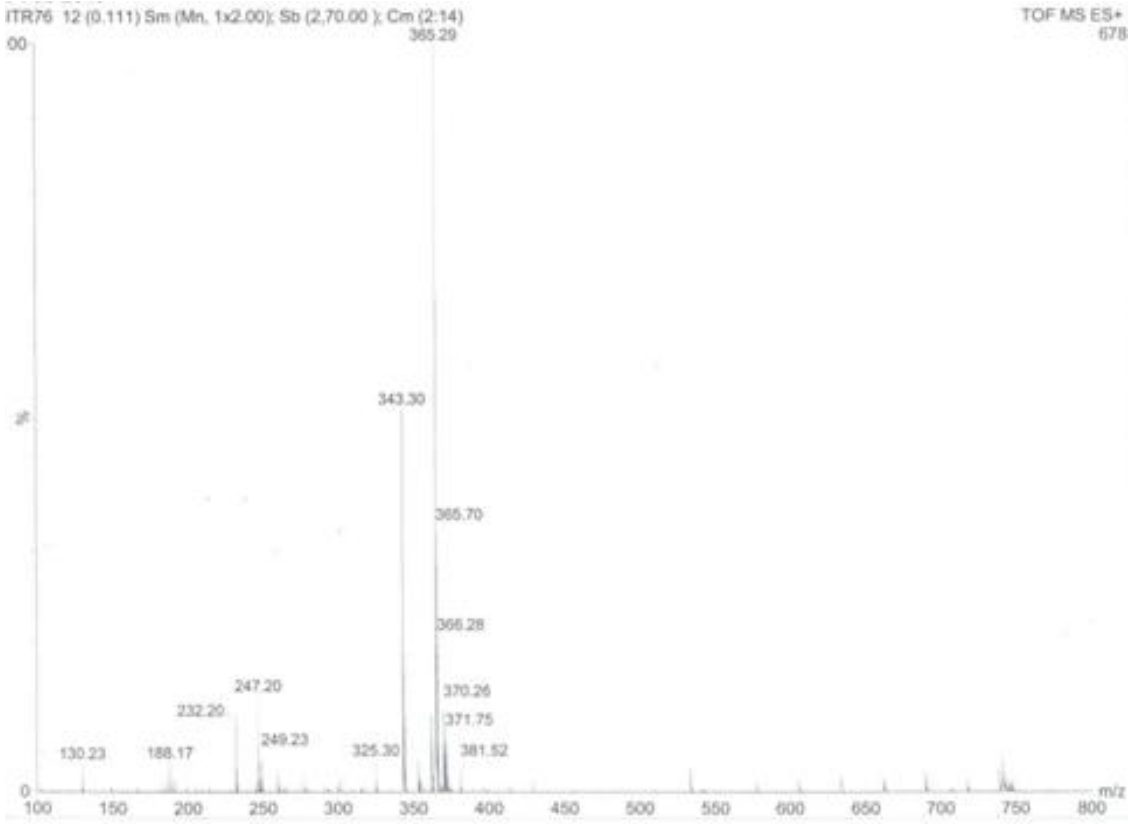

Figure S2: Mass spectrum of the ligand $\mathbf{LH_3}$.

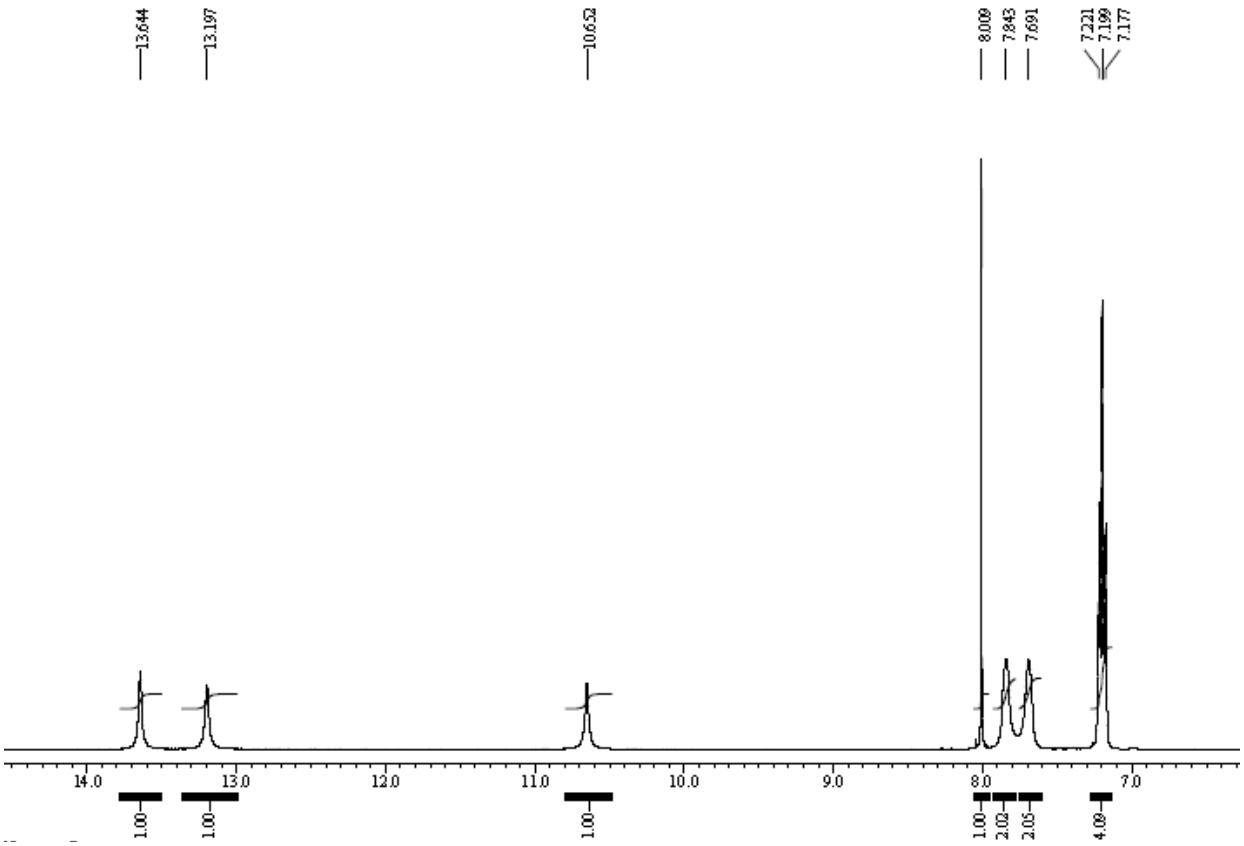

Figure S3: ^{1}H NMR spectrum of the ligand $\mathbf{LH_3}$.

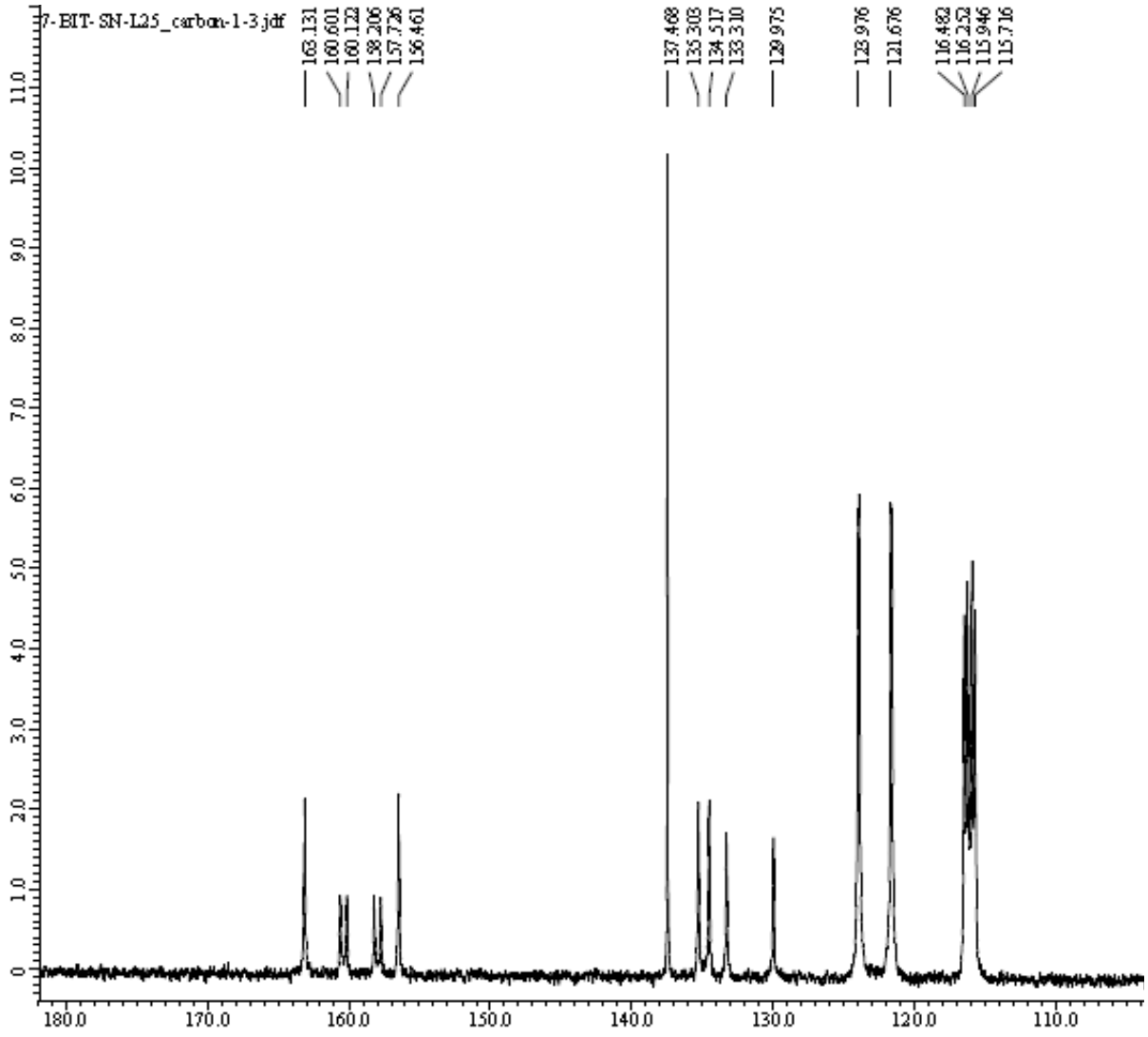

Figure S4: ^{13}C NMR spectrum of the ligand $\mathbf{LH_3}$.

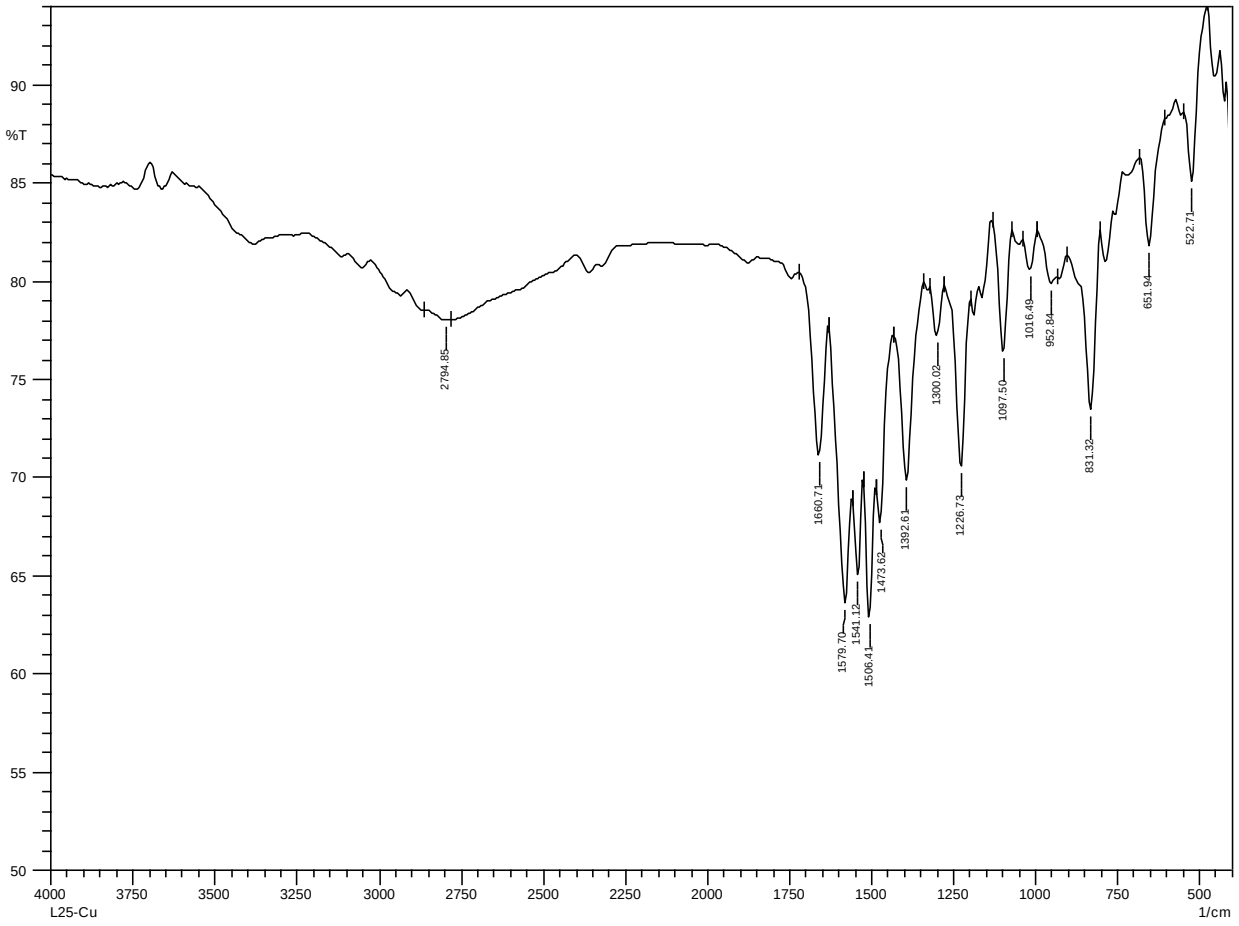

Figure S5: IR spectrum of the tetranuclear copper complex $\mathbf{Cu_4(LH)_4}$

The thermogravimetric analysis was performed on a powder sample which is devoid of the solvent molecules. The thermogram was monitored in the temperature range 30-800 ^{o}C and shows that a weight loss of 81.05% (**Figure S5**) took place in the temperature range of 200-515 ^{o}C corresponding to the loss of four molecule of amide ligand (calculated 84.27%). The rest residue is metal.

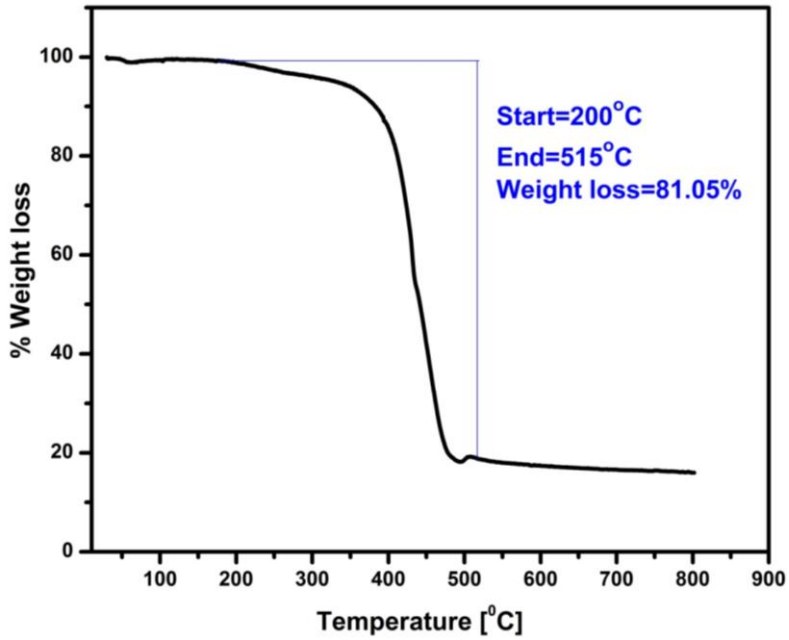

Figure S6: Thermogram of the desolvated tetranuclear copper complex [$\mathbf{Cu_4(LH)_4}$].

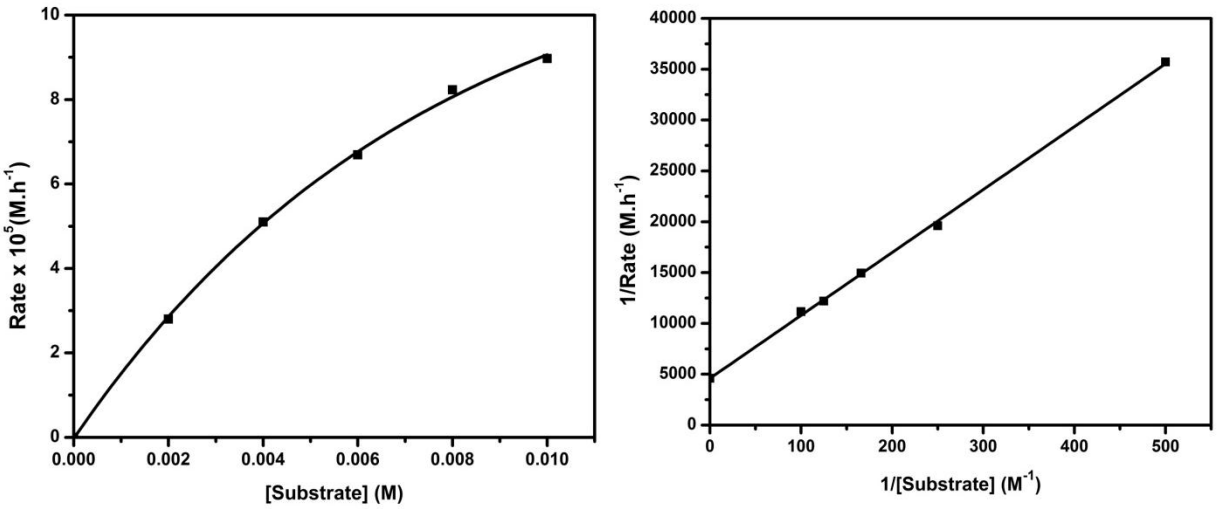

Figure S7: Plot of the initial rates versus substrate concentration for the oxidation of 3,5-DTBC catalyzed by $\mathbf{Cu_4(LH)_4}$: (a) initial rates versus substrate concentration; (b) Lineweaver−Burk plot.

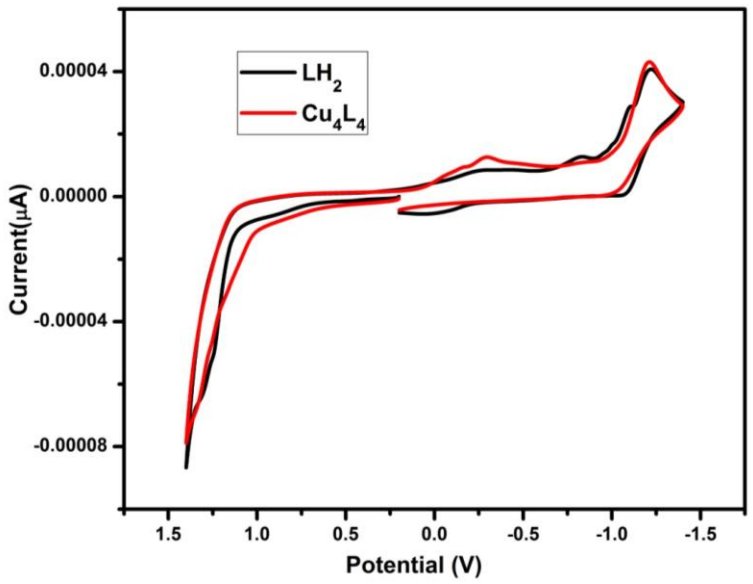

Figure S8: Cyclic voltammograms of LH_3 and $Cu_4(LH)_4$ in DMF solution, with TBAP as supporting electrolyte, in glassy carbon electrode at 100 mV/s^{-1}.

Table S1. Selected bond lengths (Å) and bond angles (°) for the tetranuclear unit **$Cu_4(LH)_4 \cdot 4DMF$**.

Bond lengths	
Cu1 N1	1.981(17)
Cu1 N8	2.000(18)
Cu1 N28[1]	1.974(19)
Cu1O42[1]	2.060(15)
Cu1O51	2.213(17)
Cu2 N3	1.981(17)
Cu2 O17	2.029(15)
Cu2 N26	1.976(18)
Cu2 N33	1.974(17)
Cu2O56	2.254(17)
Bond angles	
N1 Cu1 N8	82.50(7)
N1 Cu1 O42[1]	176.66(7)
N1 Cu1 O51	95.37(7)
N8 Cu1 O42[1]	98.51(6)
N8 Cu1 O51	95.13(7)
N28[1] Cu1 N1	97.31(7)
N28[1] Cu1 N8	163.44(8)
N28[1] Cu1 O42[1]	80.80(7)
N28[1] Cu1 O51	101.36(7)
O42[1] Cu1 O51	87.73(6)
N3 Cu2 O17	81.33 (7)
N3 Cu2O56	92.19(7)
O17 Cu2 O56	92.54(6)
N26 Cu2 N3	98.61(7)
N26 Cu2 O17	160.09(7)
N26 Cu2 O56	107.34(7)
N33 Cu2 N3	171.96(8)
N33 Cu2 O17	94.48(7)
N33 Cu2 N26	82.97(7)
N33 Cu2 O56	94.87 (7)

[1] $1 - x, 1 - y, 1 - z$

Table S2. Selected calculated spin densities for the **$Cu_4(LH)_4 \cdot 4DMF$** complex.

Atom	Spin density (in e^-)
Cu1 = Cu3[a,b]	−0.6370
Cu2 = Cu4[a,b]	+0.6353
$N1_{imid}$[a,b,c]	−0.0756
$N2_{imid}$[a,b,c]	+0.0763
$C1_{imid}$[a,b,c]	−0.0002
$C2_{imid}$[a,b,c]	+0.0017
$N1_{benz}$[a,b,d]	−0.1203
$N2_{benz}$[a,b,d]	+0.1184
$O1_{benz}$[a,b,d]	−0.0511
$O2_{benz}$[a,b,d]	+0.0483
$O1_{DMF}$[a,b,e]	−0.0020
$O2_{DMF}$[a,b,e]	+0.0003

[a] Label 1 applies for atoms attached to Cu1 and Cu3. Label 2 for atoms attached to Cu2 and Cu3. The carbon atoms appear as pair of negative and positive values. [b] Mean values. [c] Atoms of the imidazolyl moiety N-C-N. [d] Atoms of the benzamide moiety directly attached to the copper(II) ions. [e] The oxygen of the DMF solvent molecules.