Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Strategic Synthesis of [Cu_2], [Cu_4] and [Cu_5] Complexes: Inhibition and Triggering of Ligand Arm Hydrolysis and Self-aggregation by Chosen Ancillary Bridges

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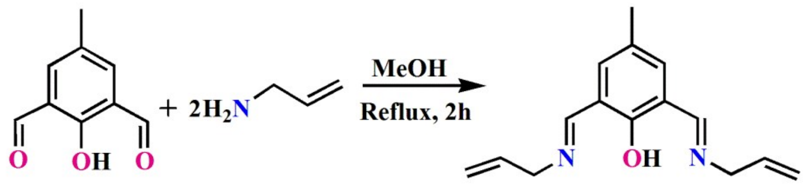
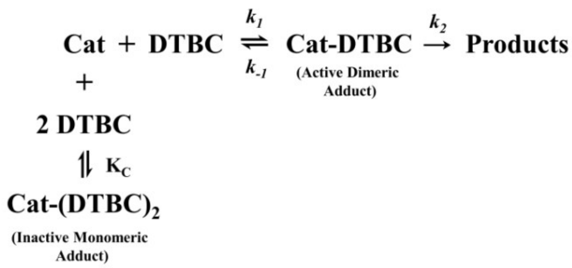


Scheme S1 Synthesis of Ligand HL1



Scheme S2 Simplified mechanism for the oxidation of 3,5-DTBC by **2** in MeOH

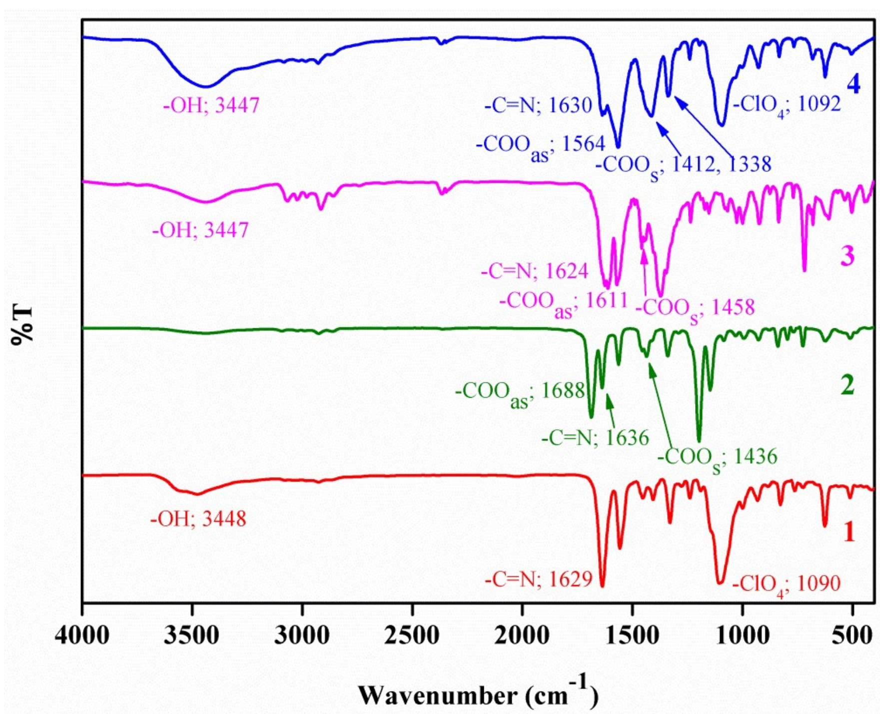


Figure S1 IR spectra of **1-4**

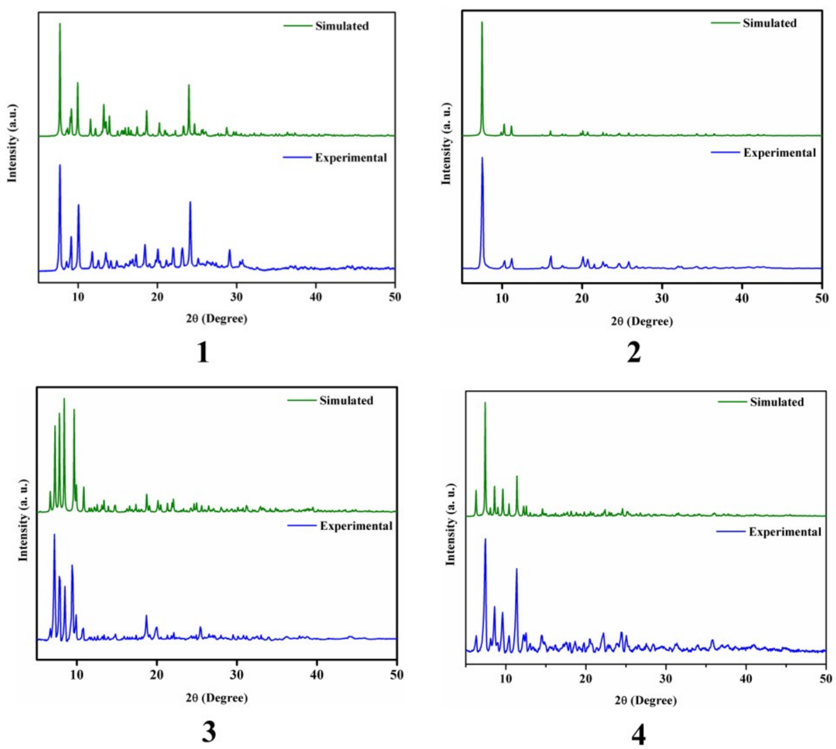


Figure S2 Powder XRD patterns of **1**-**4**

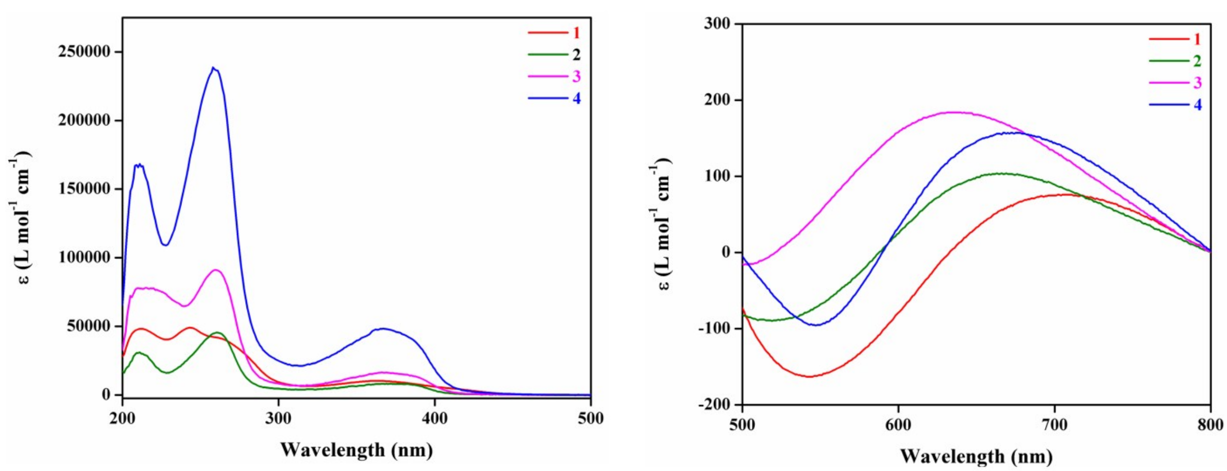


Figure S3 Charge transfer (left) and d-d transition (right) bands for **1**-**4**

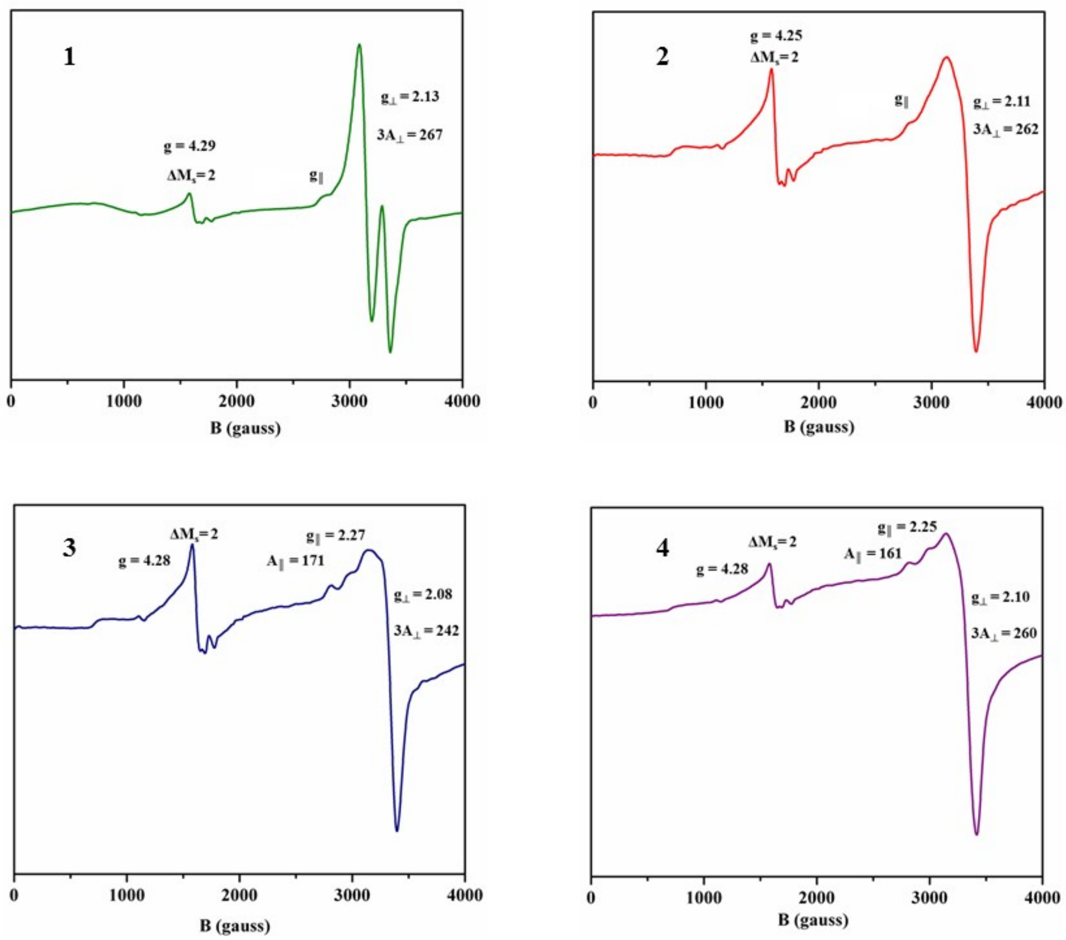


Figure S4 X-band EPR spectra of powdered samples of **1-4** at 298 K

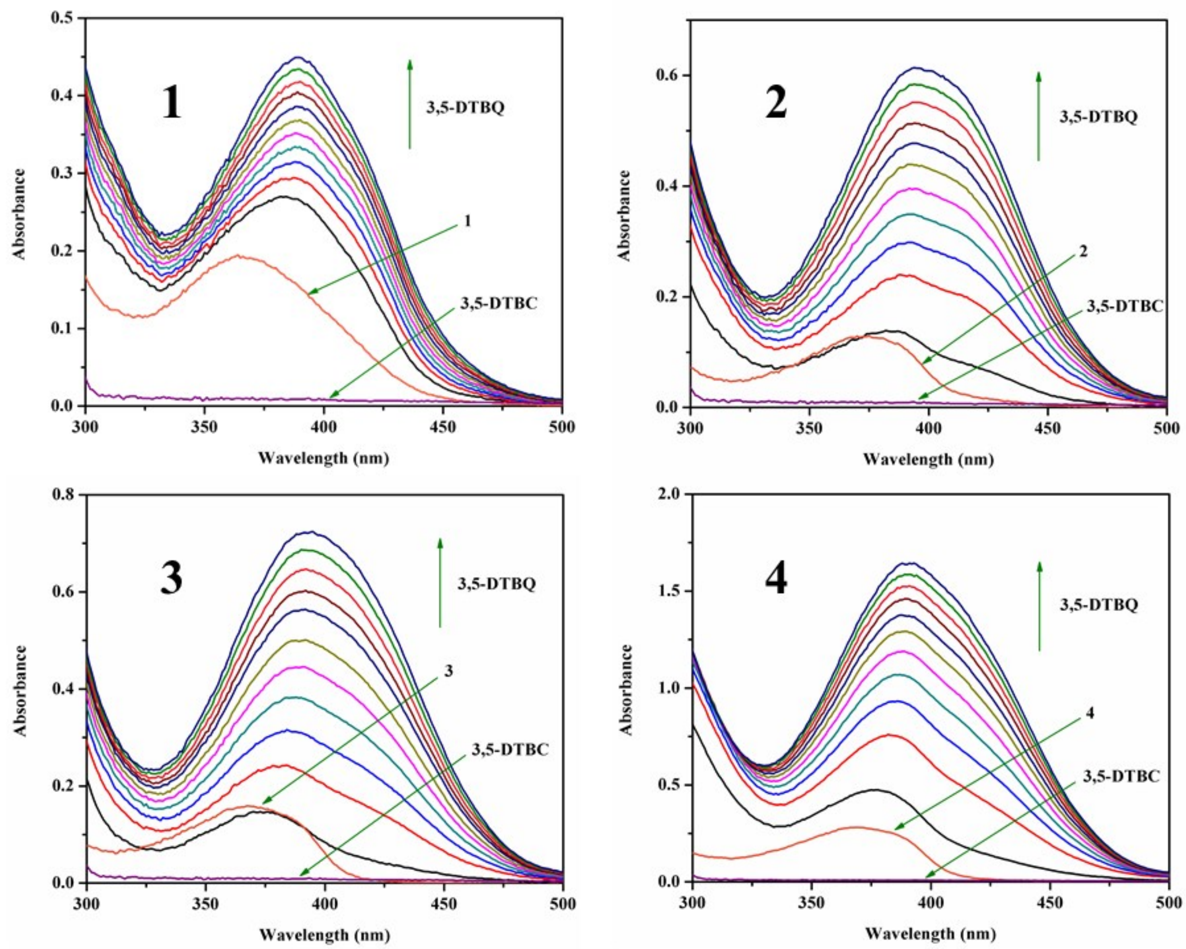


Figure S5 Time-dependent UV−vis spectral changes for **1**-**4** (concentration ~ 1 × 10^{-5} mol L^{-1}) upon addition of excess (100 fold) 3,5-$DTBCH_2$ (concentration ~ 1 × 10^{-3} mol L^{-1}) in MeOH at 298 K

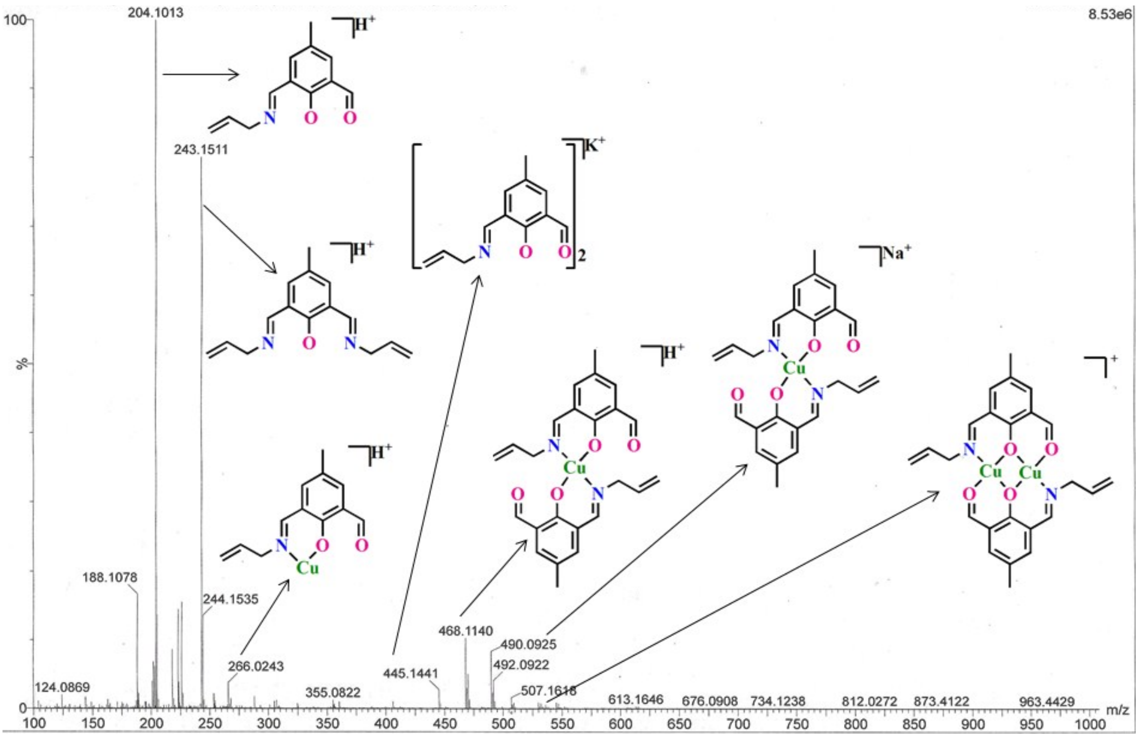


Figure S6 ESI-MS spectra of complex **1** in MeOH

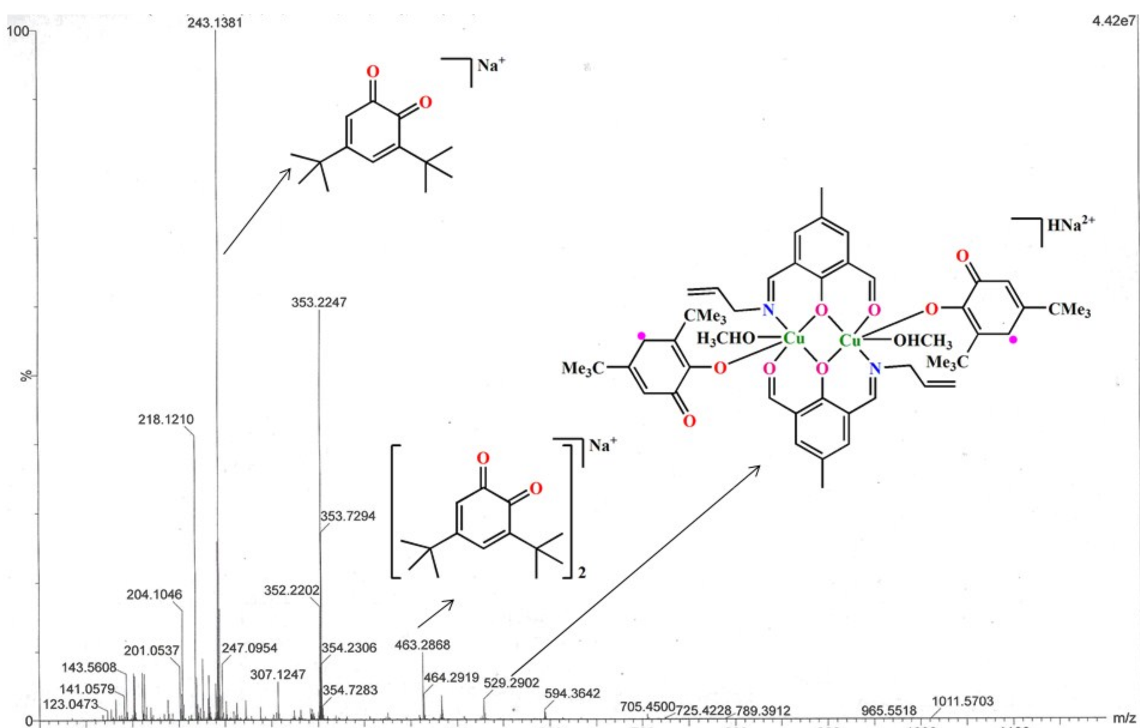


Figure S7 ESI-MS spectra of **1** and 3,5-DTBC mixture (1:100) in MeOH after 10 min of mixing

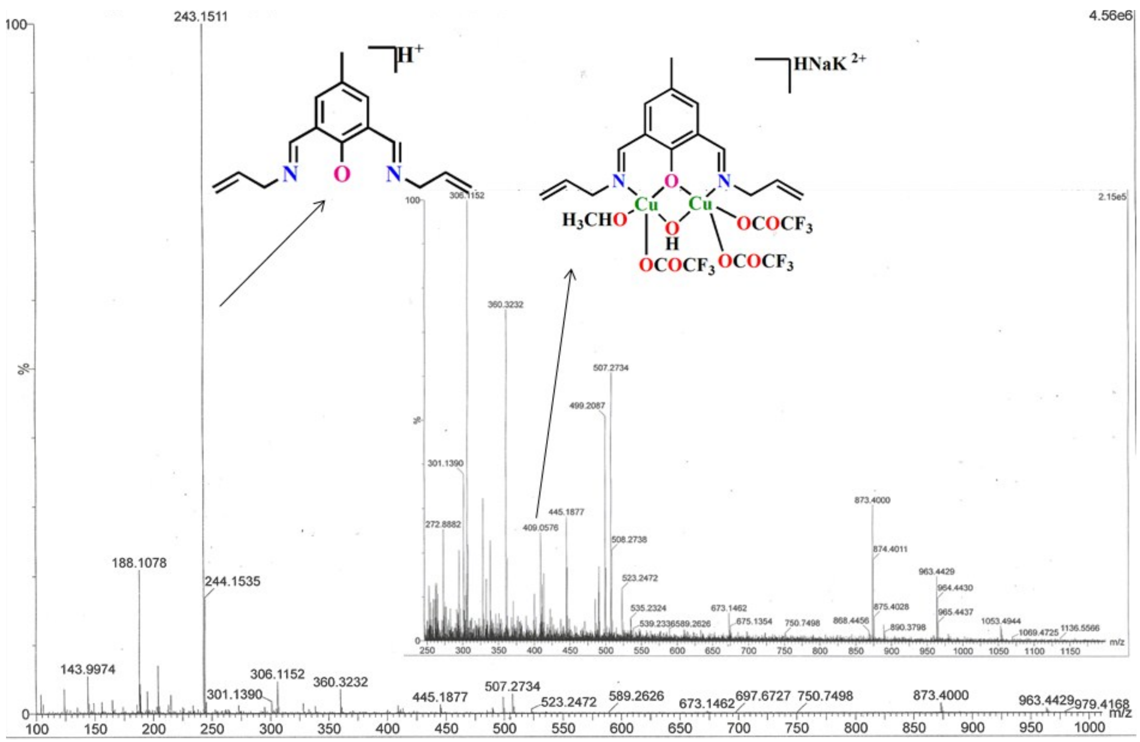


Figure S8 ESI-MS spectra of complex **2** in MeOH

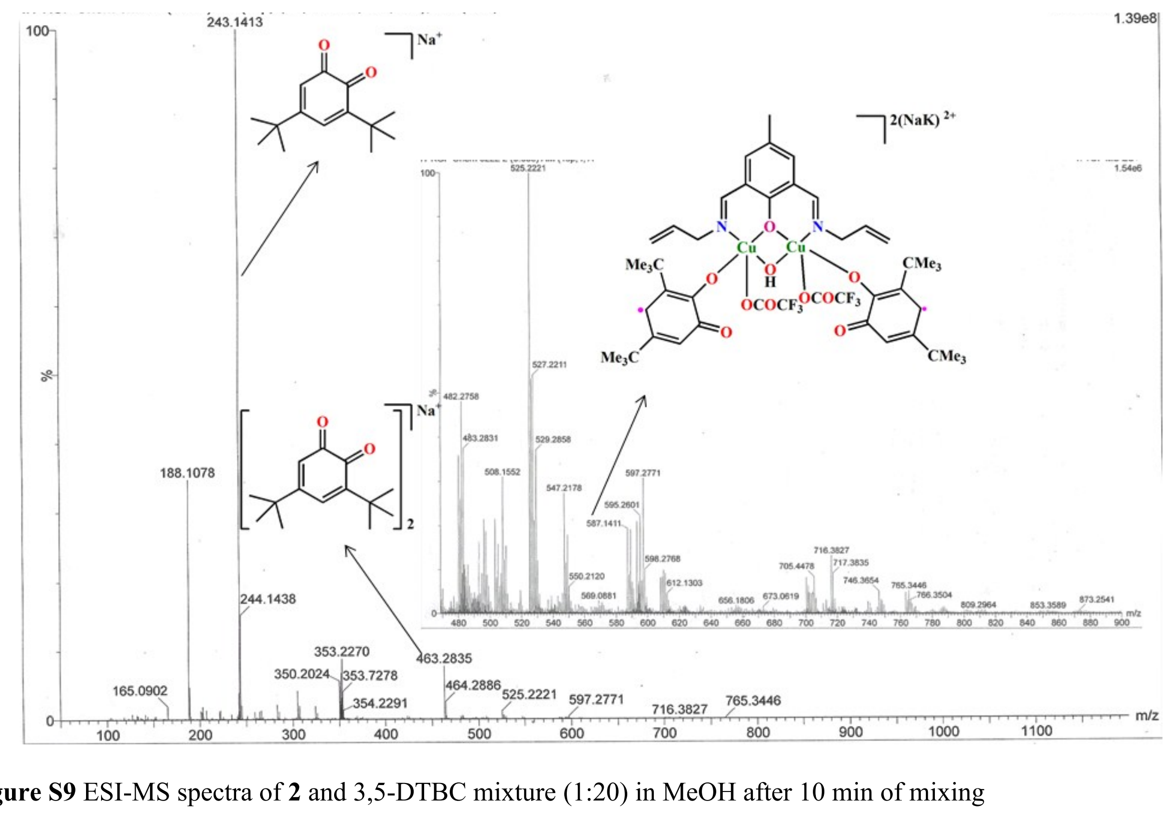


Figure S9 ESI-MS spectra of **2** and 3,5-DTBC mixture (1:20) in MeOH after 10 min of mixing

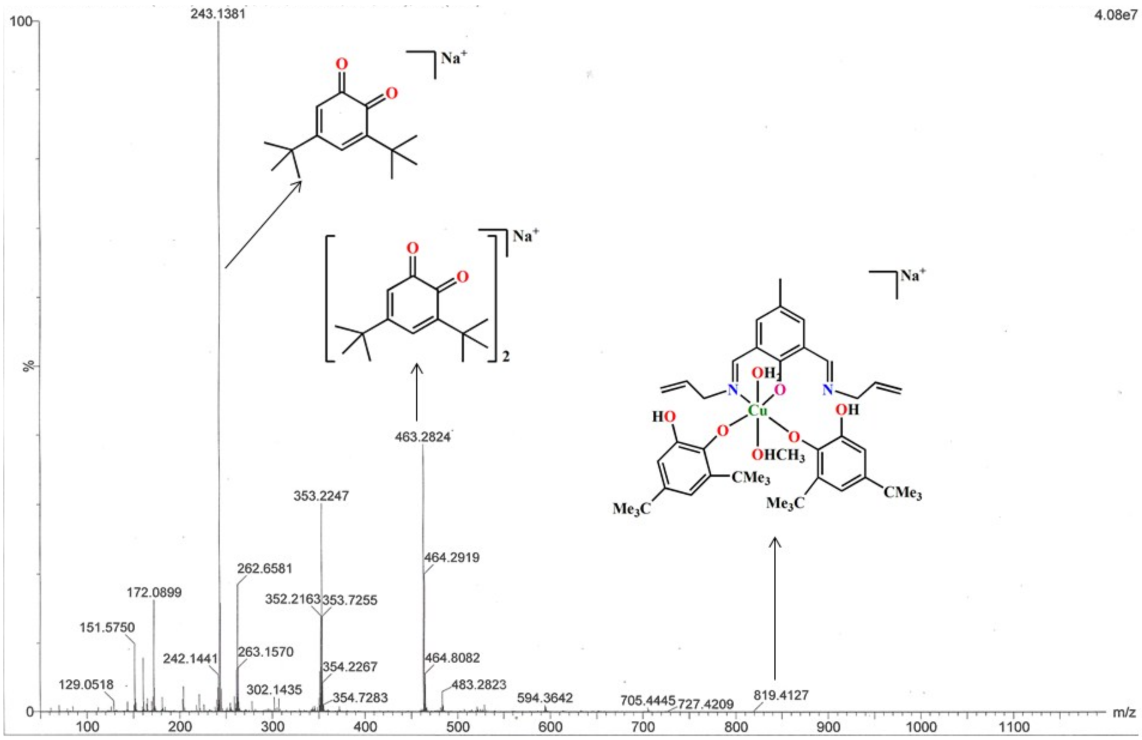


Figure S10 ESI-MS spectra of **2** and 3,5-DTBC mixture (1:100) in MeOH after 10 min of mixing

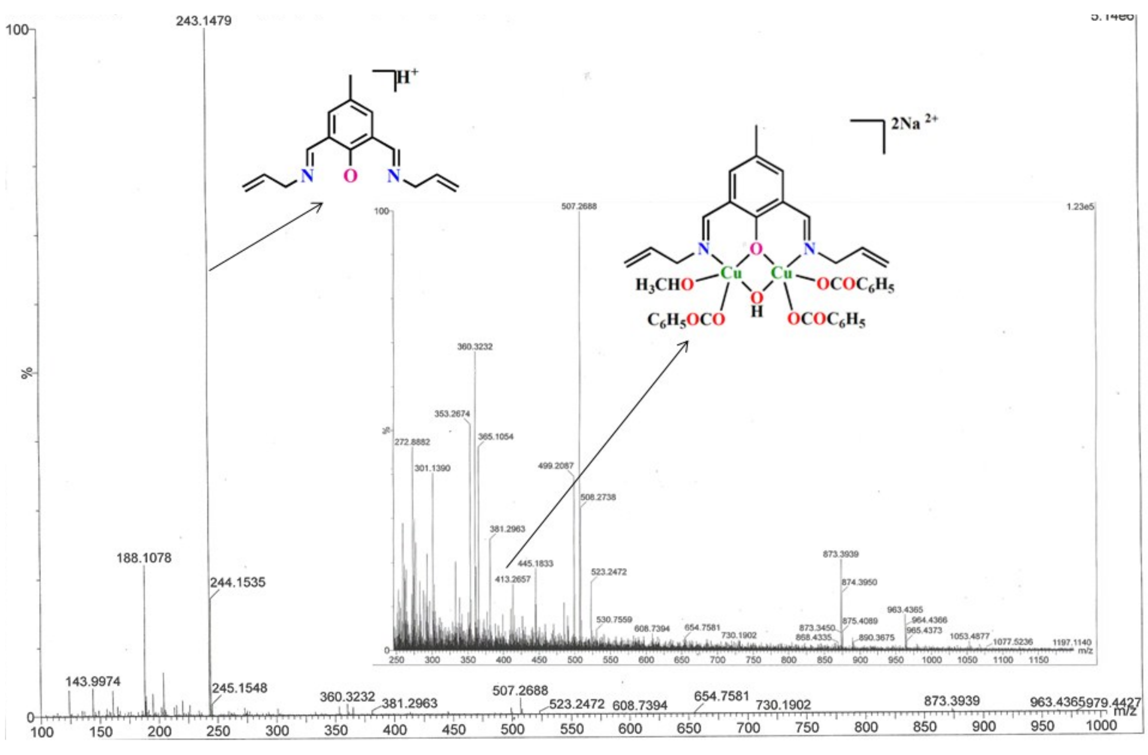


Figure S11 ESI-MS spectra of complex **3** in MeOH

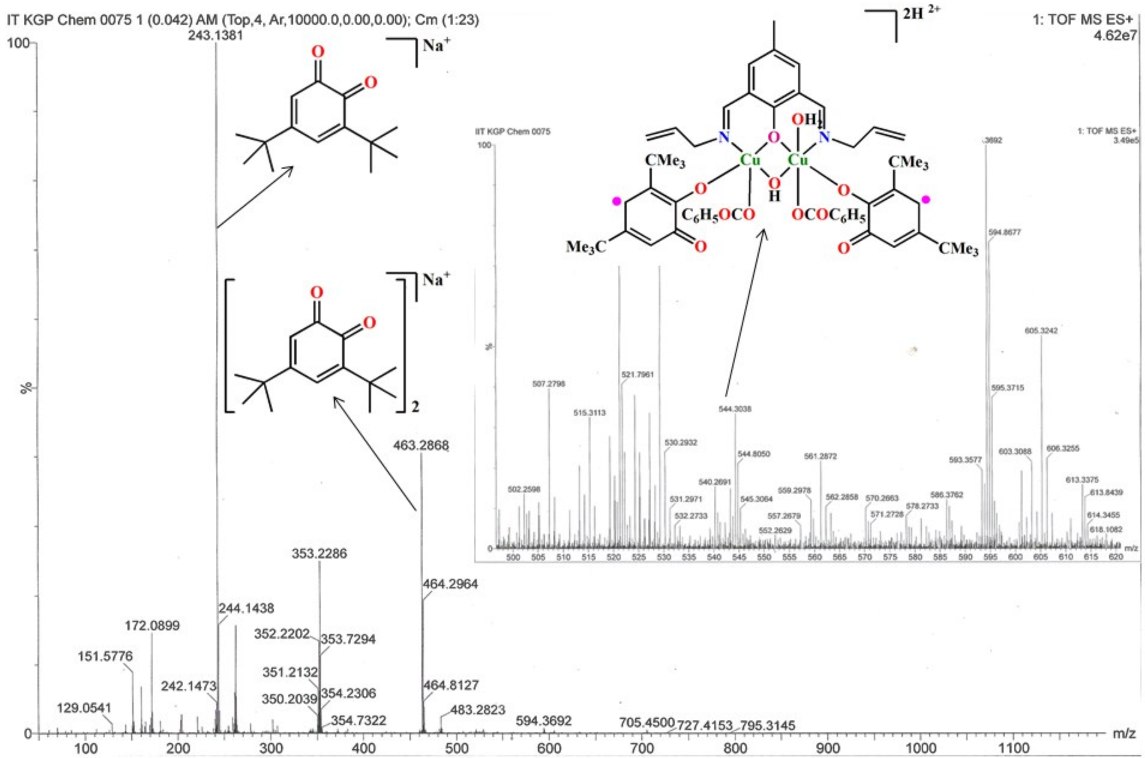


Figure S12 ESI-MS spectra of **3** and 3,5-DTBC mixture (1:100) in MeOH after 10 min of mixing

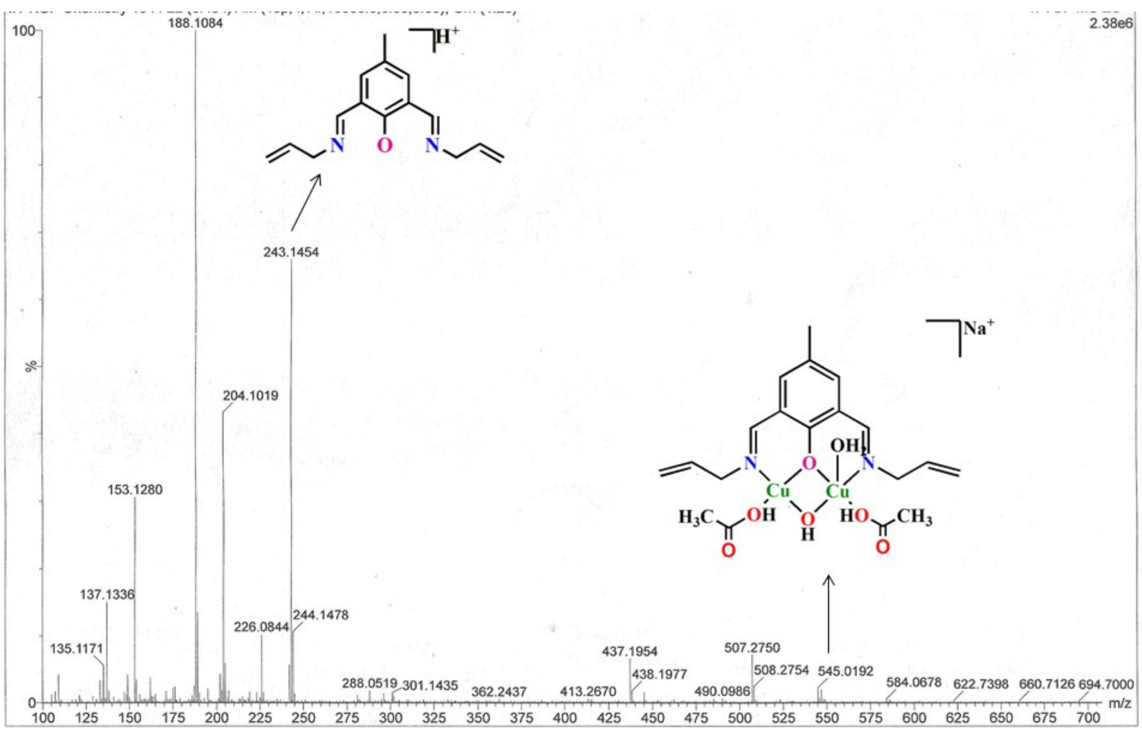


Figure S13 ESI-MS spectra of complex **4** in MeOH

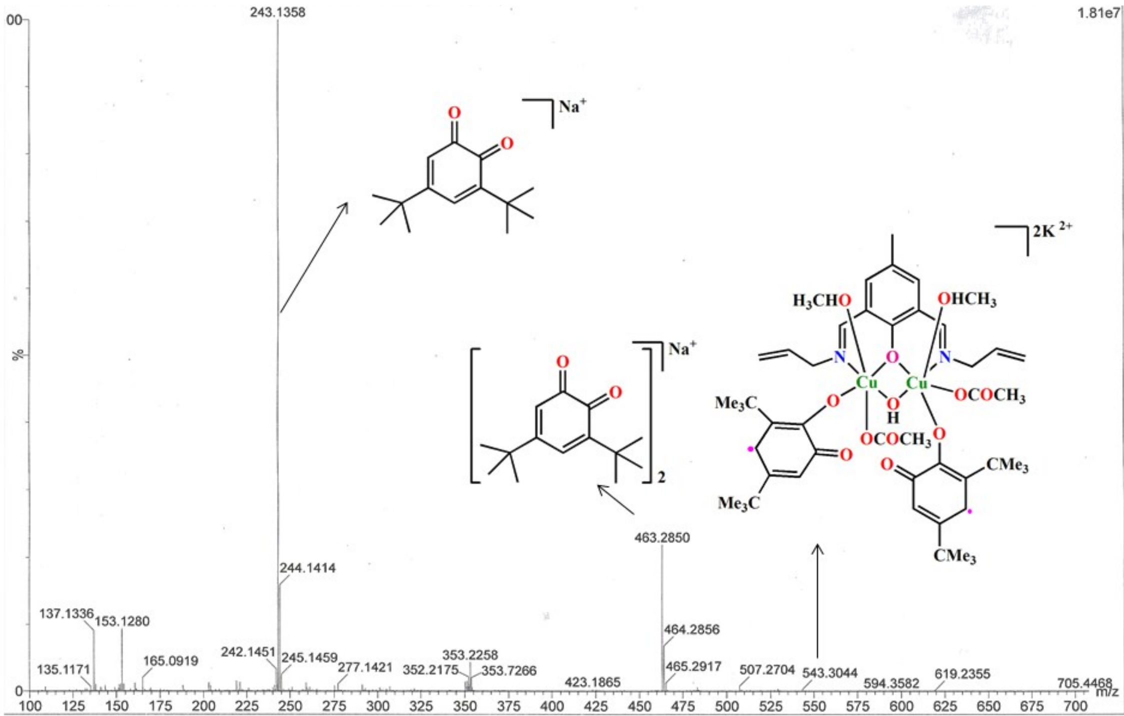


Figure S14 ESI-MS spectra of **4** and 3,5-DTBC mixture (1:100) in MeOH after 10 min of mixing

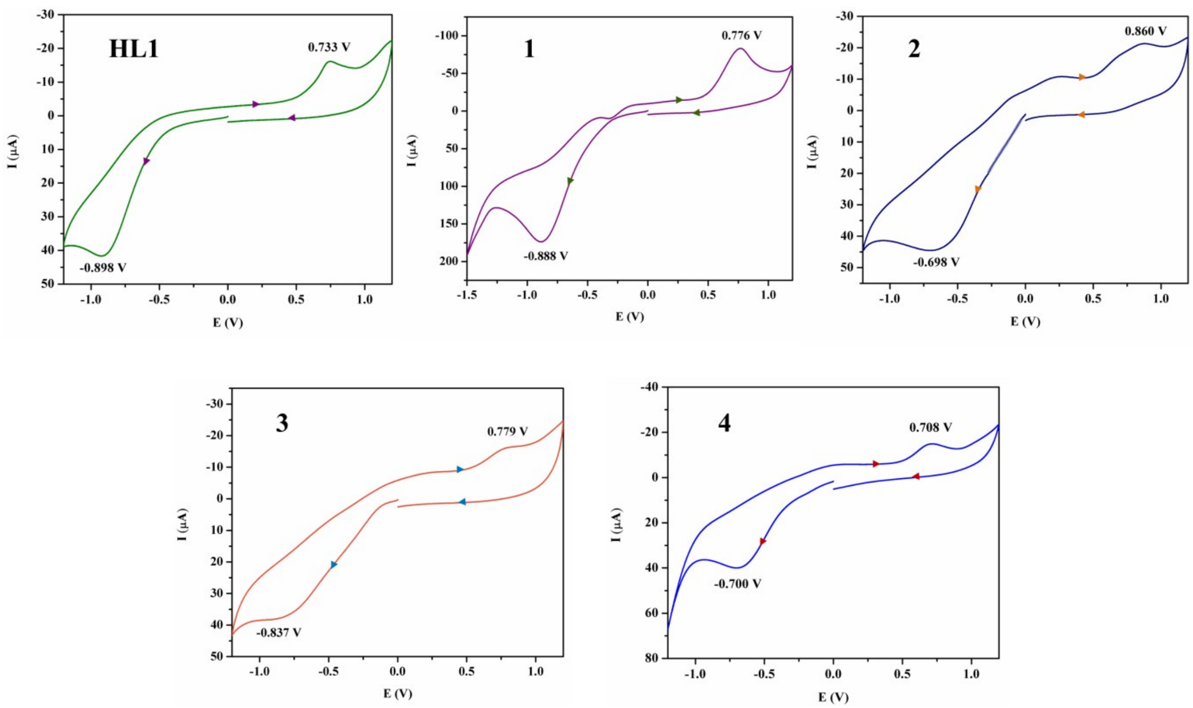


Figure S15 Cyclic voltammograms of HL1 and **1-4** in MeOH (0.1 M $^{n}Bu_4NClO_4$) at 298 K, at platinum working electrode; scan rate of 100 mV s^{-1}; Ag/AgCl reference electrode

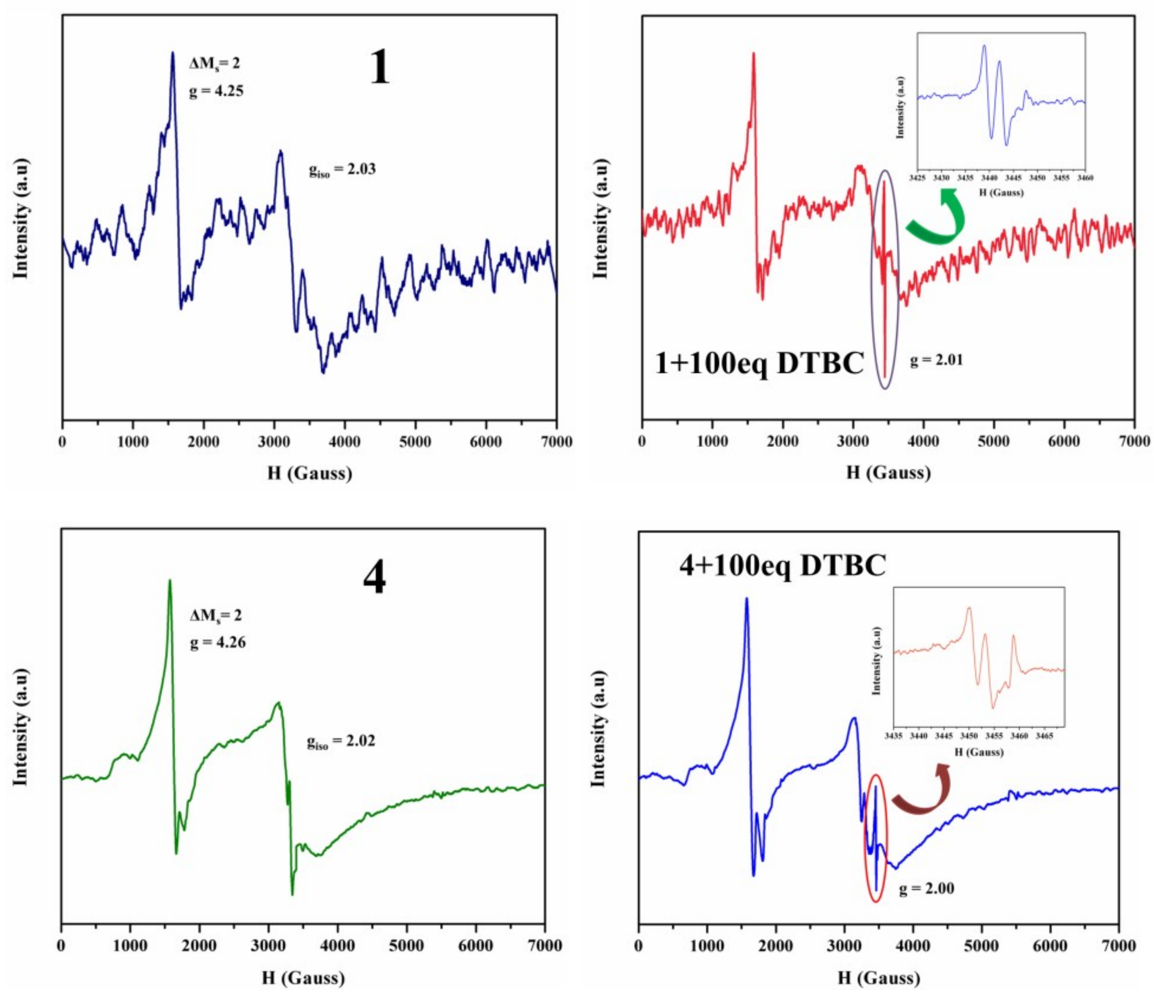


Figure S16 EPR spectra of **1** and **4** (left) and mixtures of **1** and **4** with 3,5-DTBC in 1:100 molar ratio (right) in MeOH at 298 K

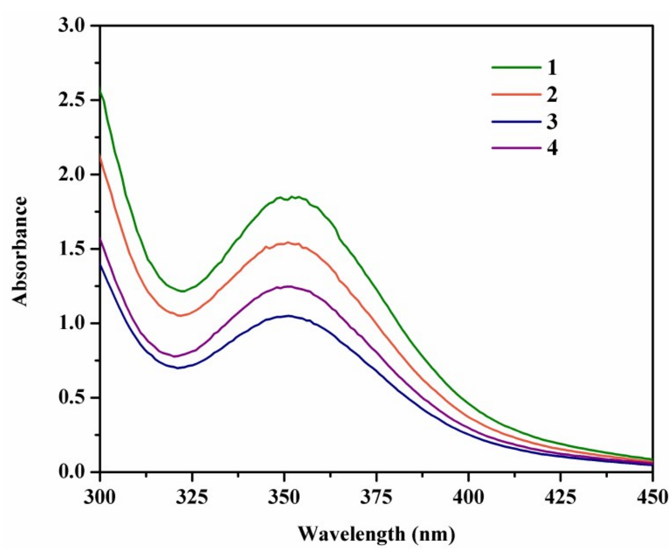


Figure S17 Absorption spectra of I_3^- confirming the generation of H_2O_2 in the system

Table S1 Selected bond lengths (Å) and angles (°) in **1**, **2**, **3** and **4**

Bond lengths (Å)					
Complex **1**					
Cu1 – O1	1.936(4)	Cu2 – O2	1.943(4)	Cu3 – O6	1.954(5)
Cu1 – O3	1.944(4)	Cu2 – O3	1.945(4)	Cu3 – O2W	2.291(5)
Cu1 – O4	1.940(5)	Cu2 – O1W	2.300(5)	Cu3 – N3	1.930(5)
Cu1 – N1	1.937(5)	Cu2 – N2	1.940(5)	Cu1 – Cu2	3.0163(9)
Cu2 – O1	1.959(4)	Cu3 – O5	1.951(4)	Cu3 – Cu3*	3.0307(12)
Complex **2**					
Cu1 – O1	1.9499(17)	Cu1 –O3	1.962(2)	Cu1 – N1	1.970(3)
Cu1 – O2	1.9290(3)	Cu1 – O4	2.342(3)	Cu1 – Cu1*	2.9979(6)
Complex **3**					
Cu1 – O1	1.999(8)	Cu2 – N2	1.965(9)	Cu4 – O11	2.334(7)
Cu1 – O2	1.913(7)	Cu3 – O2	1.935(7)	Cu4 – N4	1.963(9)
Cu1 – O4	1.935(8)	Cu3 – O3	2.009(7)	Cu1 – Cu2	3.021(2)
Cu1 – O6	2.214(9)	Cu3 – O5	2.255(8)	Cu1 – Cu3	3.193(2)
Cu1 – N1	1.992(12)	Cu3 – O7	1.954(8)	Cu1 – Cu4	3.204(2)
Cu2 – O1	1.990(8)	Cu3 – N3	1.987(11)	Cu2 – Cu3	3.286(2)
Cu2 – O2	1.908(7)	Cu4 – O2	1.924(7)	Cu2 – Cu4	3.082(2)
Cu2 – O8	2.397(7)	Cu4 – O3	1.972(7)	Cu3 – Cu4	3.0105(19)
Cu2 – O10	1.964(7)	Cu4 – O9	1.930(7)		
Complex **4**					
Cu1 – O1	1.987(4)	Cu2 – O1	1.967(5)	Cu3 – O3	1.952(4)
Cu1 – O2	1.950(5)	Cu2 – O2	1.977(4)	Cu3 – O4	1.950(4)
Cu1 – O5	1.932(4)	Cu2 – O7	1.940(5)	Cu3 – O15	1.979(5)
Cu1 – O13	2.383(5)	Cu2 – O14	2.267(5)	Cu3 – N4	1.951(6)
Cu1 – N1	1.962(6)	Cu2 – N2	1.956(6)	Cu4 – O3	1.975(5)

Cu4 – O4	1.962(4)	Cu6 – O18	1.945(4)	Cu9 – O29	1.960(5)
Cu4 – O11	1.974(5)	Cu6 – O21	1.950(5)	Cu9 – O31	2.351(6)
Cu4 – O16	2.294(5)	Cu6 – N5	1.935(6)	Cu9 – N8	1.946(6)
Cu4 – N3	1.950(6)	Cu7 – O17	1.958(5)	Cu10 – O18	1.980(4)
Cu5 – O2	1.950(4)	Cu7 – O18	1.950(5)	Cu10 – O20	1.933(5)
Cu5 – O4	1.962(4)	Cu7 – O25	1.950(5)	Cu10 – O22	2.388(6)
Cu5 – O6	2.272(5)	Cu7 – N6	1.941(7)	Cu10 – O24	1.989(5)
Cu5 – O9	2.009(5)	Cu8 – O19	1.963(5)	Cu10 – O30	1.973(5)
Cu5 – O12	1.981(5)	Cu8 – O20	1.968(4)	Cu6 – Cu7	3.0007(13)
Cu1 – Cu2	3.0442(12)	Cu8 – O27	1.917(6)	Cu8 – Cu9	3.0401(13)
Cu3 – Cu4	3.0396(13)	Cu8 – N7	1.972(6)	Cu9 – Cu10	3.0340(12)
Cu4 – Cu5	3.0090(11)	Cu9 – O19	1.969(4)		
Cu6 – O17	1.932(5)	Cu9 – O20	1.947(5)		
Bond angles (°)					
Complex **1**					
O1–Cu1–N1	93.01(19)	O3−Cu1−O4	91.91(19)	N3−Cu3−O2W	92.1(2)
O1–Cu1–O3	78.59(16)	O3−Cu2−O1W	90.6(2)	O5–Cu3–O5*	78.37(18)
O1–Cu1–O4	170.48(18)	O1−Cu2–N2	170.6(2)	O5−Cu3−O6	92.28(19)
O1–Cu2–O2	92.07(19)	O4−Cu1−N1	96.5(2)	O5−Cu3−O6*	169.69(18)
O1−Cu2–O3	78.03(16)	O1W−Cu2−N2	96.4(3)	O5−Cu3−O2W	94.9(2)
O1−Cu2−O1W	88.3(2)	Cu1−O1−Cu2	101.51(17)	O5*−Cu3−O2W	94.0(2)
O1−Cu2−N2	170.6(2)	Cu1−O3−Cu2	101.71(17)	O6−Cu3–O2W	91.1(2)
O2−Cu2−O3	169.49(19)	N3−Cu3−O5	92.87(19)	Cu3–O5–Cu3*	101.63(18)
O2−Cu2−O1W	92.7(3)	N3−Cu3−O5*	169.1(2)		
O3−Cu1−N1	170.96(19)	N3−Cu3−O6	95.9(2)		
Complex **2**					
O1–Cu1–O2	78.77(6)	O1−Cu1−O3	172.22(9)	O1−Cu1−O4*	86.20(8)

O1–Cu1–N1	91.77(10)	O2−Cu1−N1	165.07(8)	N1−Cu1−O4*	94.52(10)
O2–Cu1–O3	94.65(7)	O3−Cu1−O4*	90.45(11)	Cu1−O1−Cu1*	100.48(12)
O2–Cu1–O4*	96.32(6)	O3−Cu1−N1	95.50(11)	Cu1−O2−Cu1**	113.328(10)
Complex **3**					
O1–Cu1–N1	90.8(4)	O2−Cu3−O5	95.8(3)	O6−Cu1−N1	95.6(5)
O1–Cu1–O2	78.4(3)	O2−Cu3−O7	96.4(3)	O7−Cu3−N3	91.9(4)
O1–Cu1–O4	165.4(3)	O2–Cu4–N4	169.8(3)	O8−Cu2−N2	83.2(3)
O1–Cu1–O6	88.0(3)	O2–Cu4–O3	80.2(3)	O8−Cu2−O10	112.8(3)
O1−Cu2–N2	90.5(4)	O2–Cu4–O9	93.3(3)	O9−Cu4–N4	95.0(3)
O1–Cu2–O2	78.7(3)	O2−Cu4−O11	92.4(3)	O9−Cu4−O11	110.3(3)
O1–Cu2–O8	85.1(3)	O3−Cu3–N3	90.9(4)	O10−Cu2–N2	96.2(4)
O1–Cu2–O10	161.5(3)	O3−Cu3–O5	85.9(3)	O11−Cu4−N4	90.3(3)
O2–Cu1–N1	163.4(5)	O3−Cu3–O7	172.9(3)	Cu1−O1–Cu2	98.4(3)
O2−Cu1–O4	94.8(3)	O3−Cu4−N4	90.3(3)	Cu1−O2–Cu2	104.5(3)
O2−Cu1–O6	96.7(3)	O3–Cu4–O9	164.5(3)	Cu1−O2–Cu3	112.2(3)
O2−Cu2–N2	169.2(4)	O3–Cu4–O11	84.2(3)	Cu1−O2−Cu4	113.2(4)
O2−Cu2–O8	96.7(3)	O4−Cu1−N1	92.8(4)	Cu2−O2–Cu3	117.5(4)
O2−Cu2–O10	93.8(3)	O4−Cu1−O6	104.7(3)	Cu2−O2–Cu4	107.1(3)
O2−Cu3–N3	159.6(4)	O5−Cu3−N3	101.1(4)	Cu3−O2−Cu4	102.6(3)
O2−Cu3−O3	79.0(3)	O5–Cu3–O7	100.0(3)	Cu3−O3–Cu4	98.3(3)
Complex **4**					
O1–Cu1–N1	92.5(2)	O1−Cu2−O7	171.54(18)	O2−Cu2−O7	93.53(19)
O1–Cu1–O2	78.43(18)	O1−Cu2−O14	93.1(2)	O2−Cu2−O14	92.07(19)
O1–Cu1–O5	174.3(2)	O2–Cu1–N1	167.6(2)	O2−Cu5−O4	173.21(18)
O1–Cu1–O13	89.49(17)	O2–Cu1–O5	96.08(19)	O2–Cu5–O6	94.03(17)
O1−Cu2–N2	92.2(2)	O2−Cu1–O13	89.83(18)	O2−Cu5−O9	96.06(19)
O1–Cu2–O2	78.27(18)	O2–Cu2–N2	166.6(3)	O2−Cu5−O12	87.31(19)

O3−Cu3−N4	93.7(2)	O16−Cu4–N3	94.7(2)	O19−Cu9−O20	77.99(19)
O3−Cu3−O4	78.53(18)	Cu1−O1–Cu2	100.7(2)	O19−Cu9−O29	169.8(2)
O3–Cu3–O15	166.4(2)	Cu1−O2–Cu2	101.6(2)	O19−Cu9−O31	91.3(2)
O3−Cu4−N3	93.2(2)	Cu1−O2–Cu5	108.0(2)	O20−Cu8−N7	170.1(2)
O3–Cu4–O4	77.72(18)	Cu2−O2–Cu5	113.4(2)	O20−Cu8−O27	92.0(2)
O3–Cu4–O11	169.94(19)	Cu3−O3–Cu4	101.43(19)	O20−Cu9−N8	169.0(2)
O3–Cu4–O16	90.12(19)	Cu3−O4–Cu4	101.99(18)	O20−Cu9−O29	93.2(2)
O4−Cu3–N4	169.3(2)	Cu3−O4–Cu5	108.3(2)	O20−Cu9−O31	88.5(3)
O4−Cu3–O15	90.20(18)	Cu4−O4–Cu5	100.2(2)	O20−Cu10−O22	96.1(2)
O4−Cu4−N3	168.1(2)	O17–Cu6–N5	93.7(3)	O20−Cu10−O24	84.77(19)
O4–Cu4–O11	92.53(18)	O17−Cu6−O18	78.79(19)	O20−Cu10−O30	91.2(2)
O4–Cu4–O16	92.96(19)	O17−Cu6−O21	166.7(2)	O21−Cu6−N5	97.7(3)
O4–Cu5–O6	92.46(17)	O17–Cu7–N6	92.7(3)	O22−Cu10−O24	97.8(2)
O4–Cu5–O9	86.26(18)	O17−Cu7−O18	78.0(2)	O22−Cu10−O30	89.6(2)
O4−Cu5–O12	90.46(18)	O17−Cu7−O25	168.7(2)	O24–Cu10–O30	172.0(2)
O5−Cu1–N1	92.7(2)	O18−Cu6−N5	170.3(3)	O25−Cu7−N6	97.9(3)
O5−Cu1–O13	91.85(19)	O18−Cu6–O21	90.6(2)	O27−Cu8−N7	97.9(2)
O6–Cu5–O9	87.19(19)	O18−Cu7–N6	166.4(3)	O29−Cu9−N8	95.7(2)
O6–Cu5–O12	91.91(19)	O18−Cu7–O25	92.11(19)	O29−Cu9−O31	93.8(2)
O7–Cu2–N2	95.5(2)	O18−Cu10−O20	178.1(2)	O31−Cu9−N8	97.3(3)
O7–Cu2–O14	89.2(2)	O18−Cu10−O22	85.4(2)	Cu6−O17−Cu7	100.9(2)
O9–Cu5–O12	176.56(18)	O18−Cu10−O24	96.16(19)	Cu6−O18−Cu7	100.8(2)
O11−Cu4–N3	96.1(2)	O18−Cu10−O30	87.6(2)	Cu6−O18–Cu10	108.2(2)
O11−Cu4–O16	92.88(19)	O19−Cu8−N7	92.5(2)	Cu7−O18−Cu10	110.0(2)
O13−Cu1–N1	98.7(2)	O19−Cu8−O20	77.65(19)	Cu8−O19−Cu9	101.3(2)
O14−Cu2−N2	97.9(2)	O19−Cu8−O27	166.7(2)	Cu8−O20–Cu9	101.9(2)
O15–Cu3–N4	98.4(2)	O19−Cu9−N8	92.5(2)	Cu8−O20–Cu10	112.1(2)

O9–Cu20–O10	102.9(2)				