

Supporting Information

Dinuclear Complexes of Copper and Zinc with *m*-Xylene/Cyclohexane- Linked bis-Aspartic Acids: Synthesis, Characterization, Dioxygen Activation, and Catalytic Oxidation of Nitrobenzene in Pure Aqueous Solution

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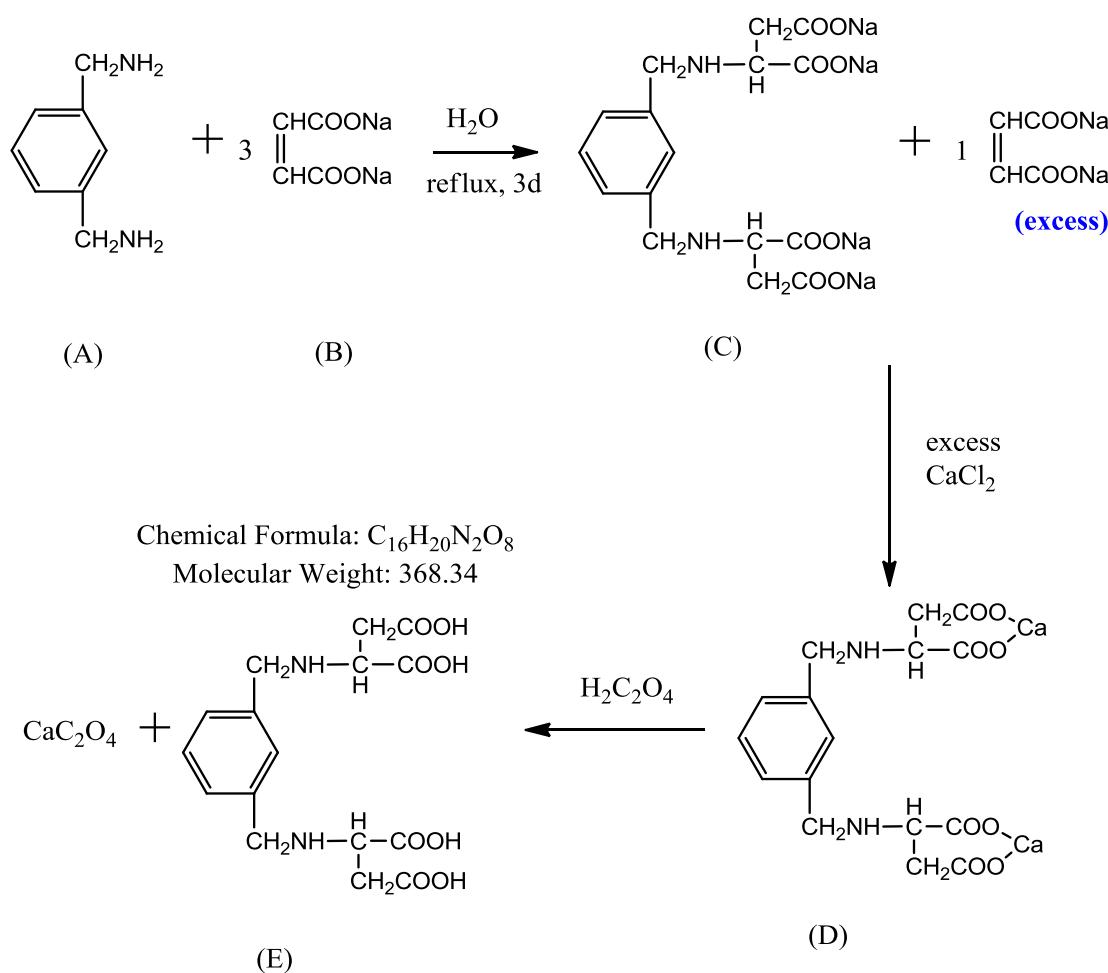
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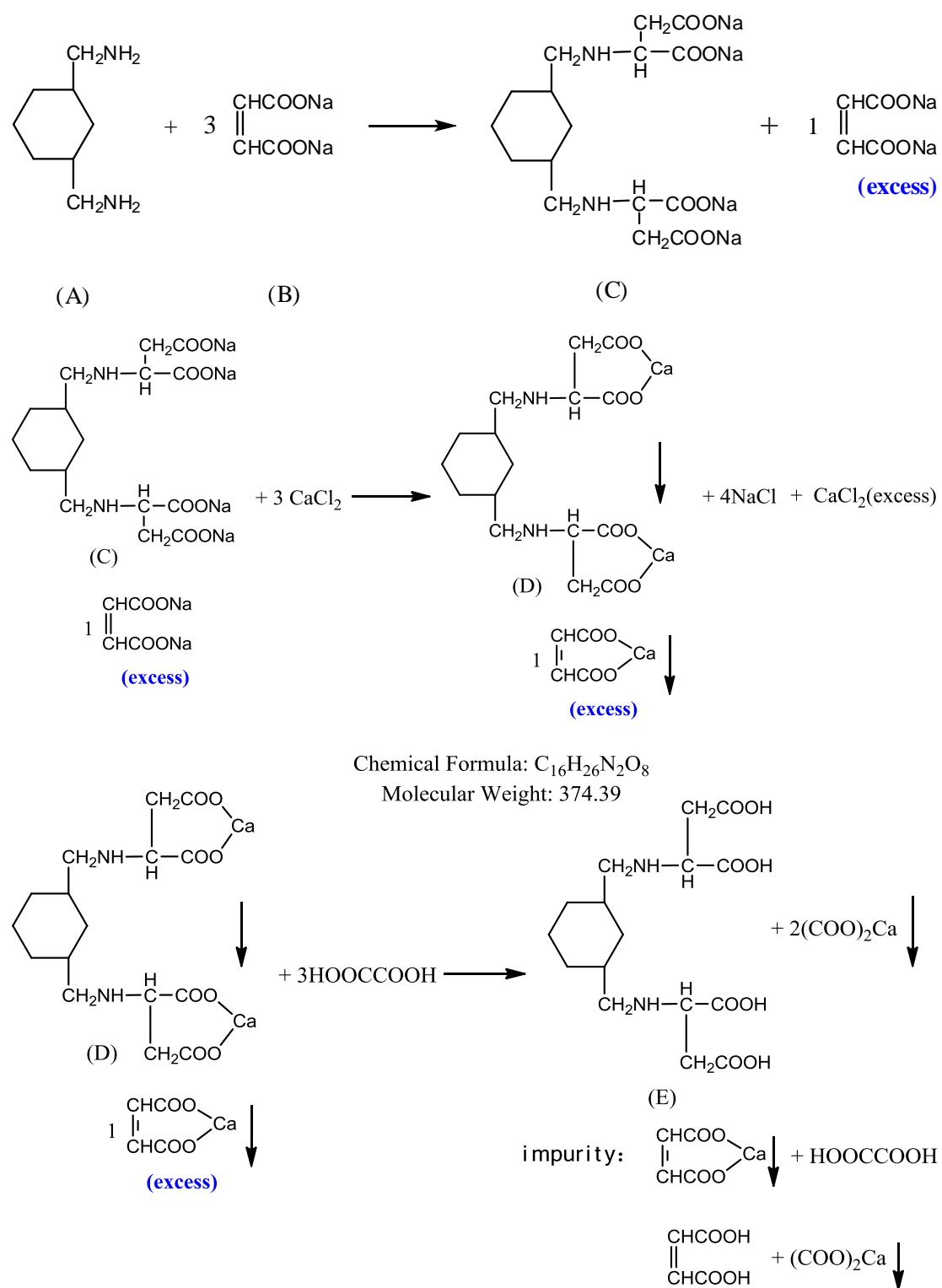
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Synthetic procedure of the ligands



Scheme s1. Synthetic procedure of ligand L_b



Scheme s2. Synthetic procedure of ligand Lc

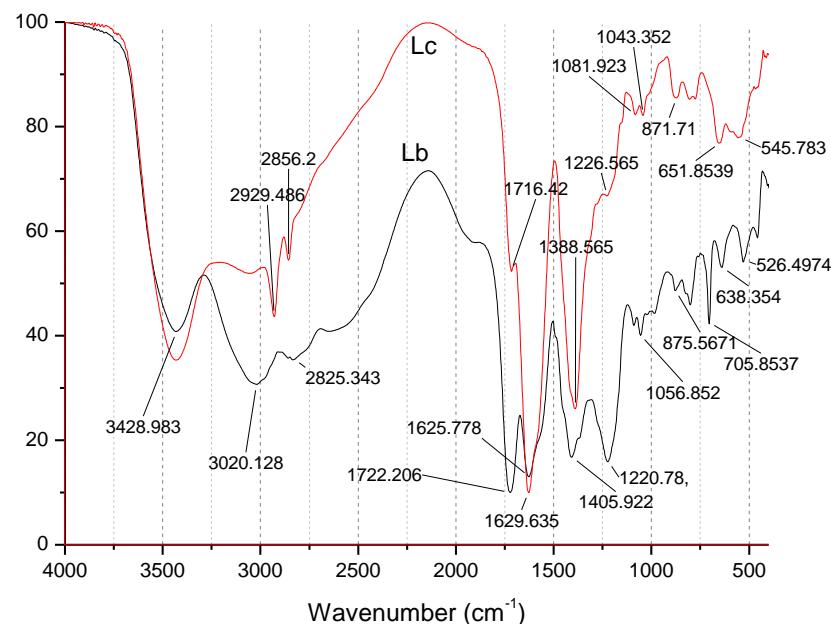
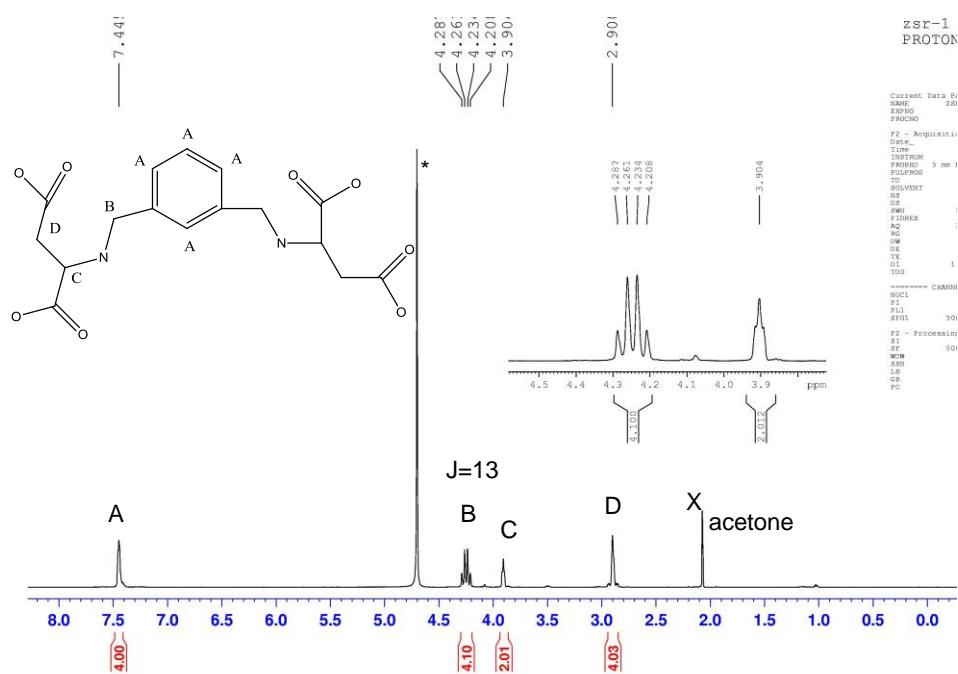


Fig. s1. IR spectra of ligand Lb and Lc (KBr disc)



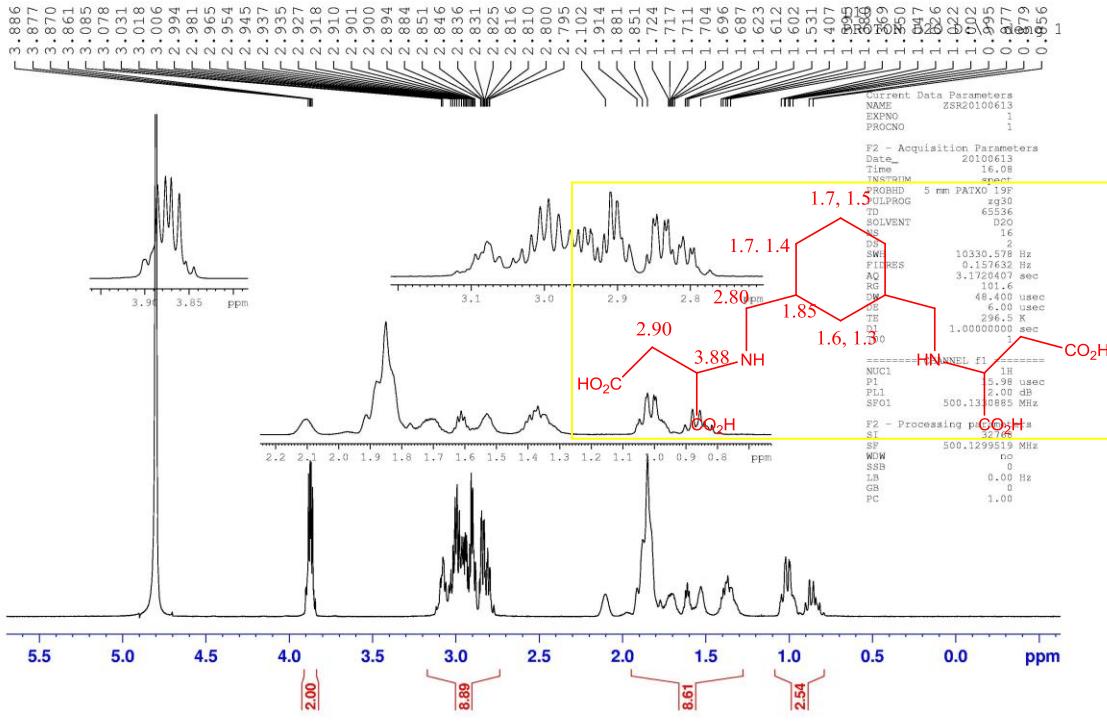


Fig. s3. ^1H NMR of Lc in D_2O

20100802-1
C13CPD D20

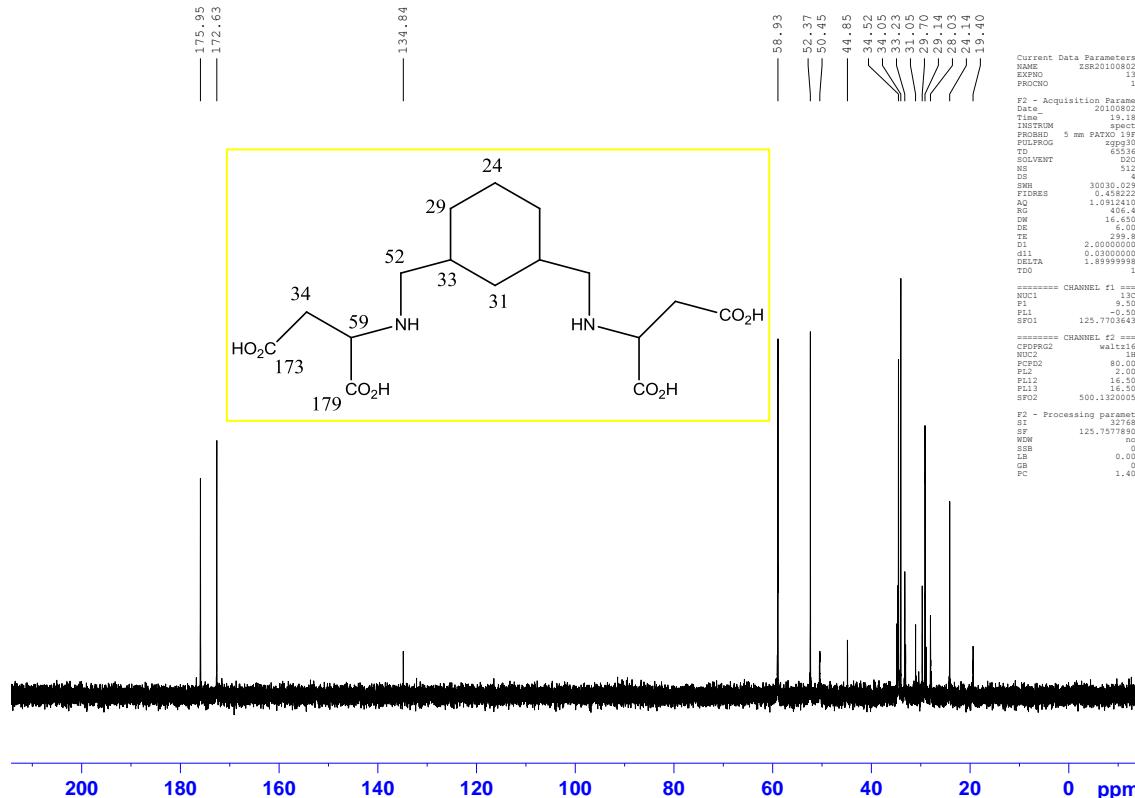
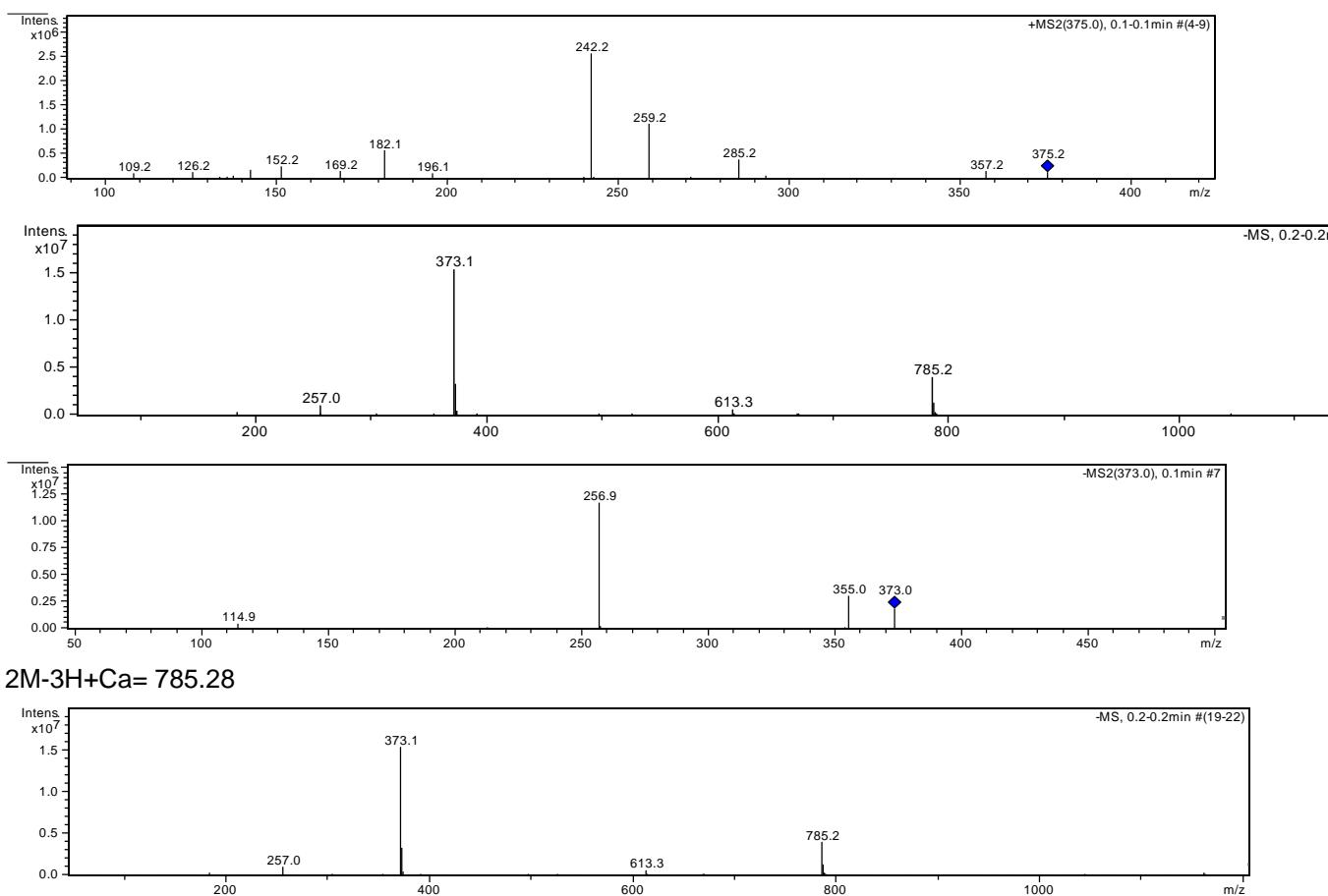
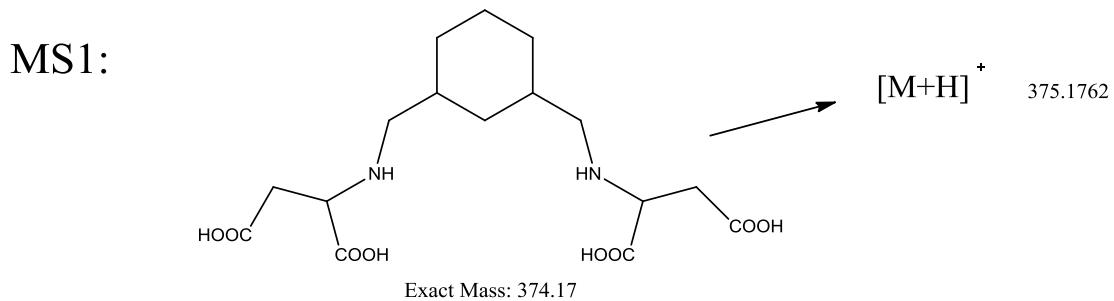


Fig. s4. ^{13}C NMR of L_c in D_2O



2M-3H+Ca= 785.28

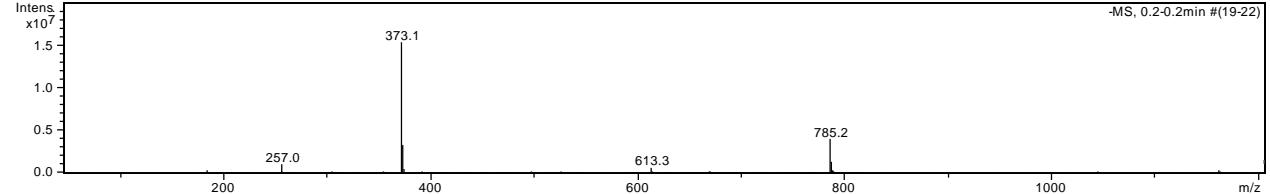


Fig. s5 EI-MS spectra of Lc in aqueous solution

MS2:

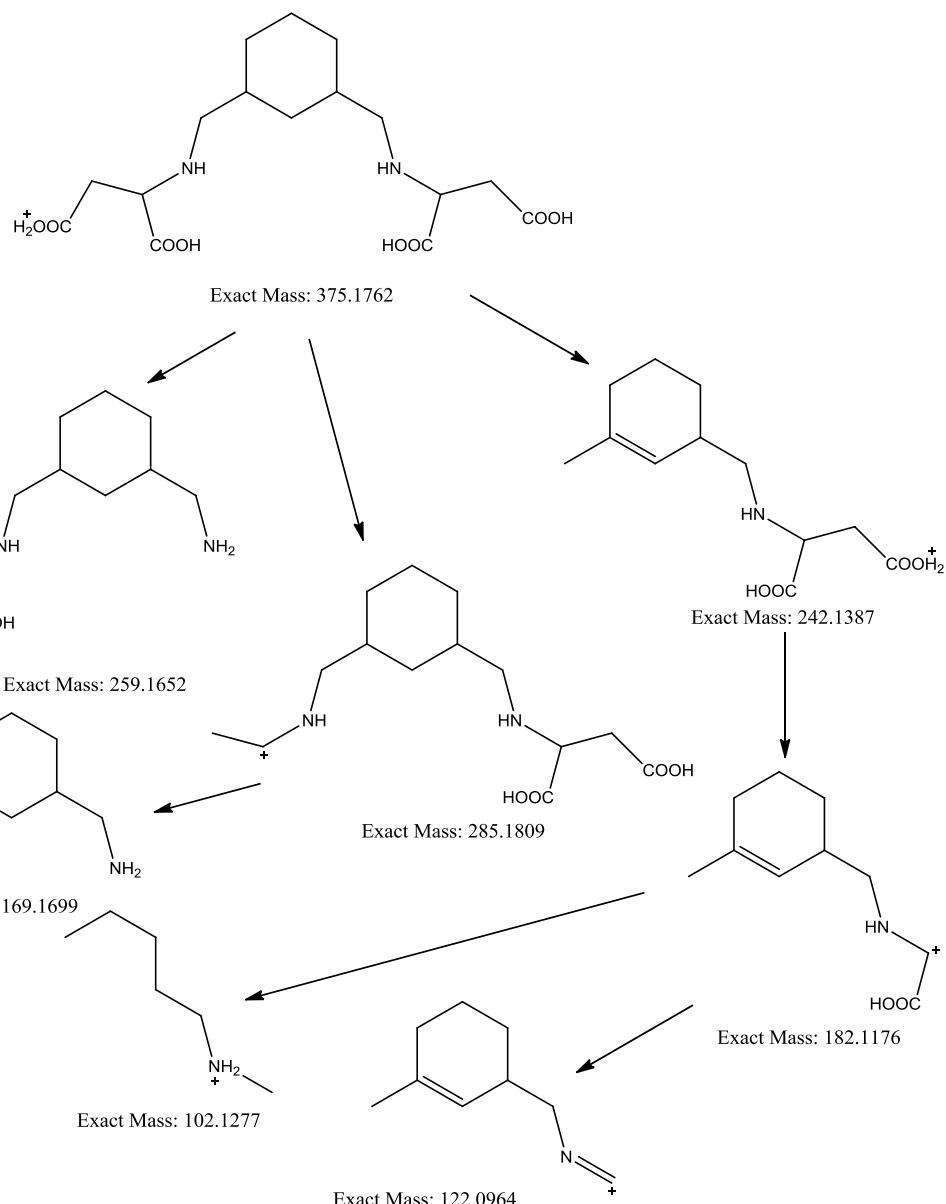


Fig. s6 Ionization mode of Lc in positive MS spectrum

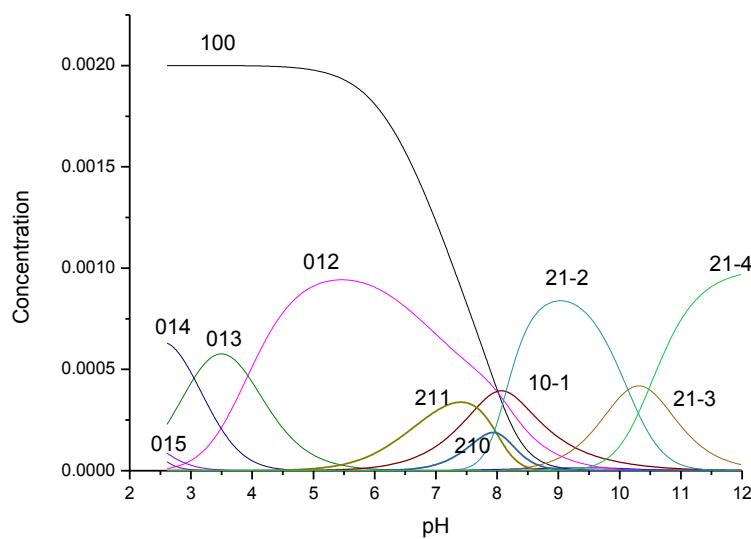
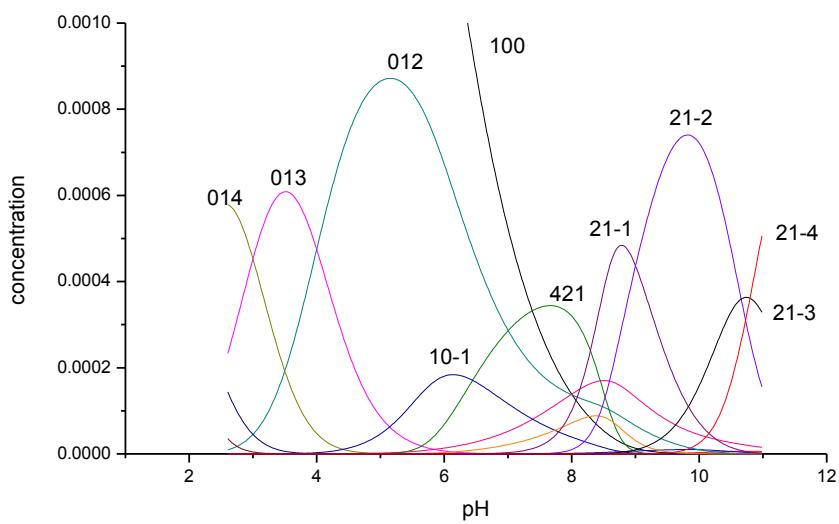


Fig. s7 Distribution curve of 1.00×10^{-3} M ligand and 2.00×10^{-3} M $\text{Zn}(\text{NO}_3)_2$ in aqueous solution at 25°C , $I=0.10$ M KNO_3 . top: L_b ; bottom: L_c

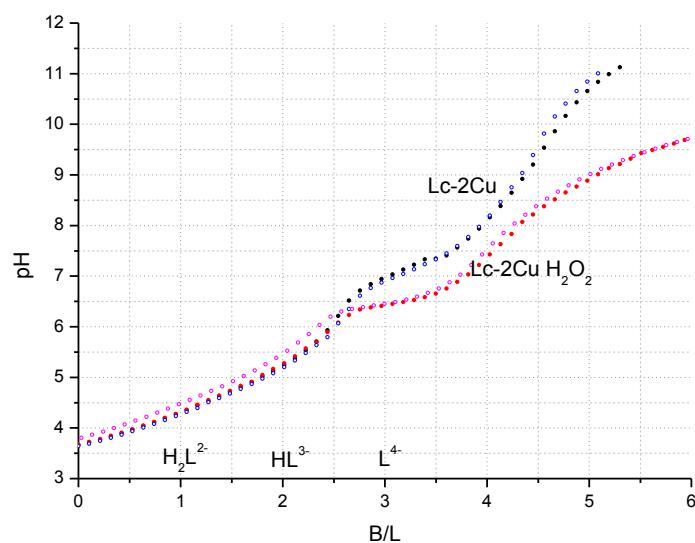


Fig. s8 pH titration curve of 1.000×10^{-3} M Cu₂-Lc in absence and presence of 10.00 eq H₂O₂ at 25.0 ± 0.1 °C, I=0.10 M KNO₃. B/L is the molar ration of base to ligand.

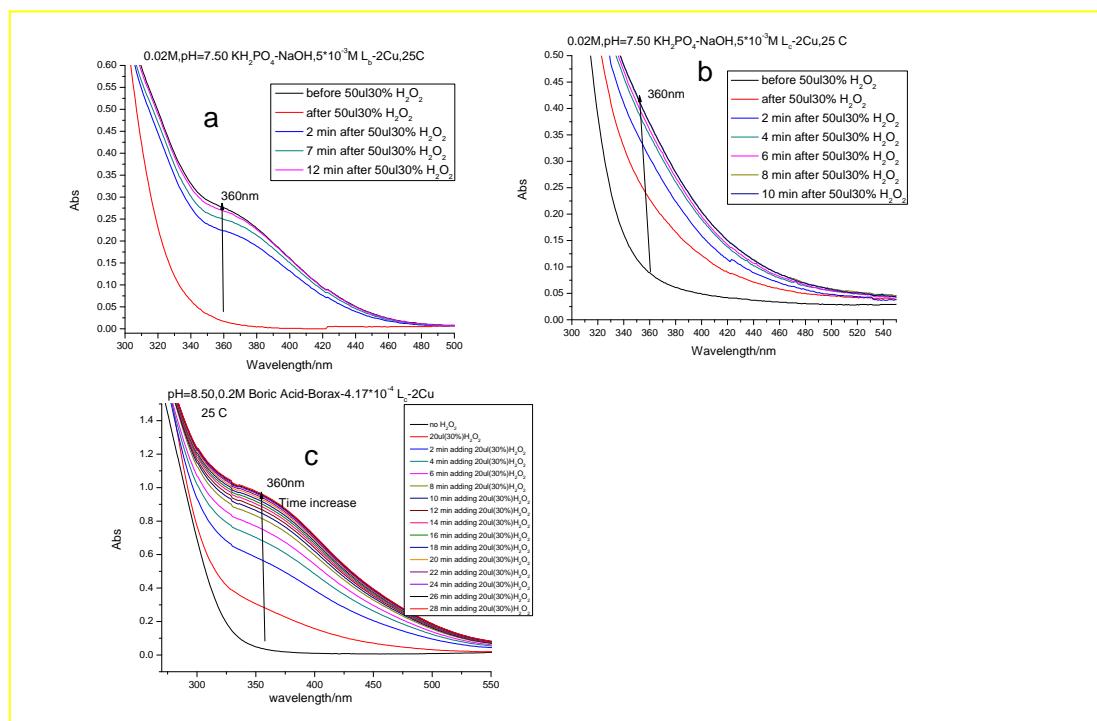


Fig. s9 Spectral changes recorded for the reaction of 5.0×10^{-3} M L_b-2Cu (a) and Lc-2Cu (b) with 0.25 M H₂O₂ in pH=7.50, 0.02 M KH₂PO₄-NaOH-solution at 25 C. In pH 8.5 borax buffer, the spectral changes for Lc-2Cu reaction with H₂O₂ is much larger (c).

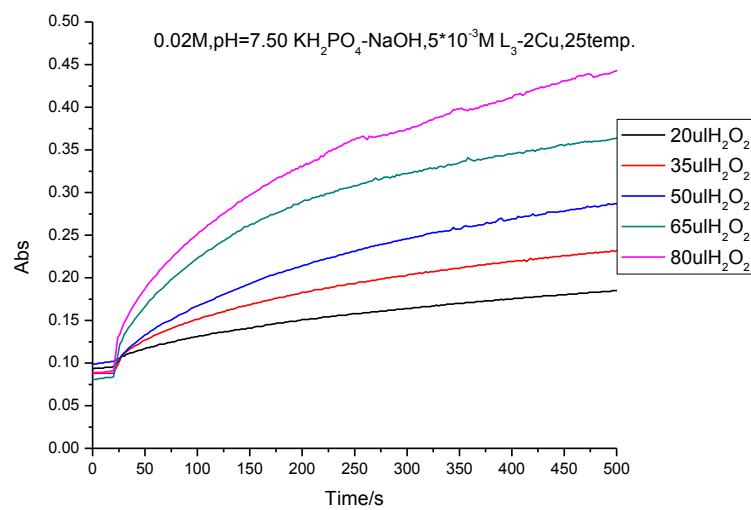
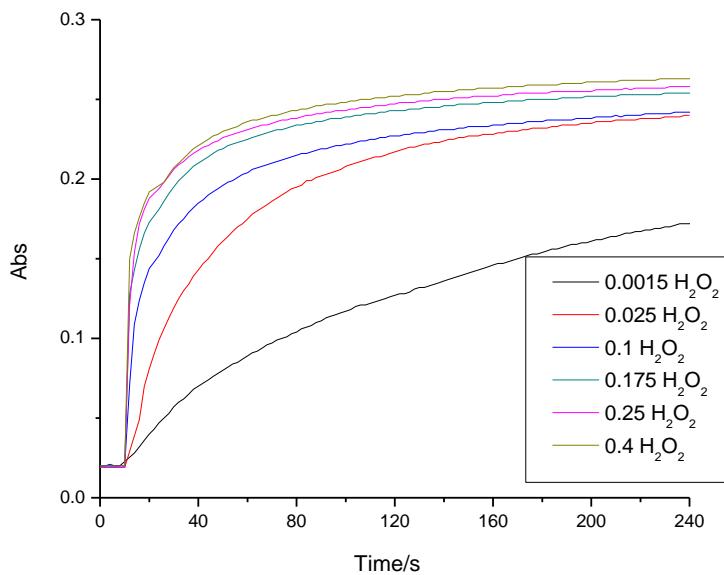


Fig. s10 Time dependence of 360 nm absorbance for the reaction of 5.0×10^{-4} M L-2Cu with different concentration H_2O_2 in 0.02 M KH_2PO_4 -NaOH buffer solution at 25C, pH=7.50. Top: Lb-2Cu complex; Bottom: Lc-2Cu complex

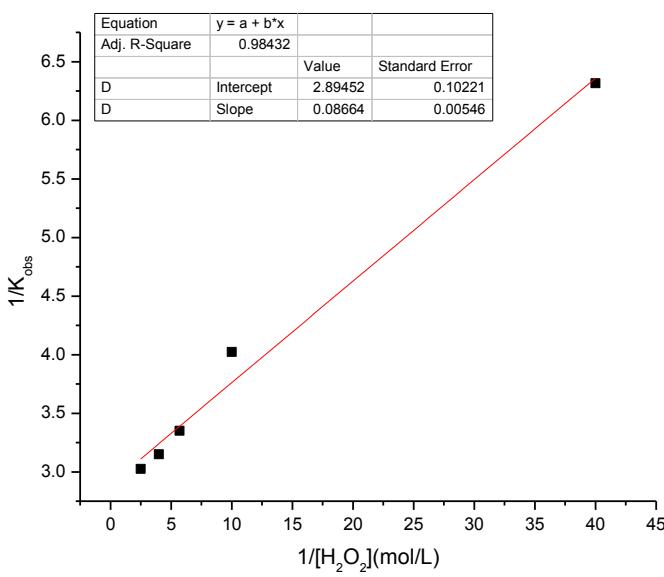
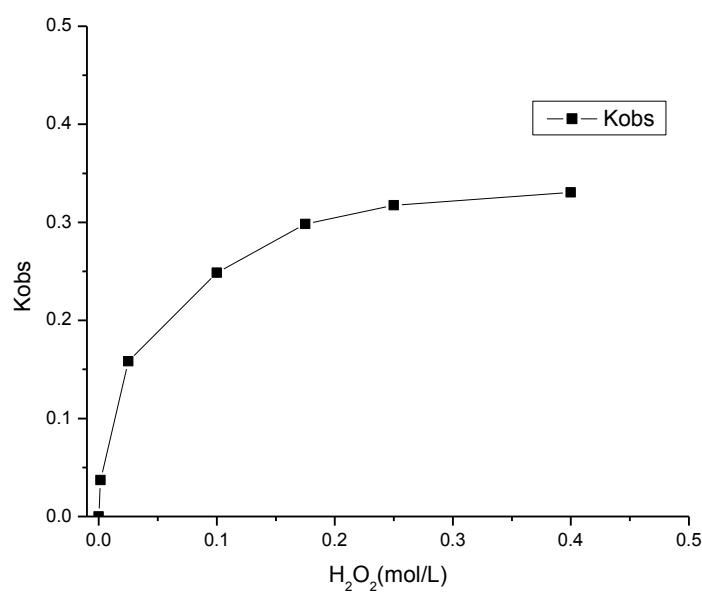


Fig. s11 Plot of the observed second-order rate constants determined at 360 nm as a function of $[\text{H}_2\text{O}_2]$ for $\text{L}_c\text{-}2\text{Cu}$ complexes

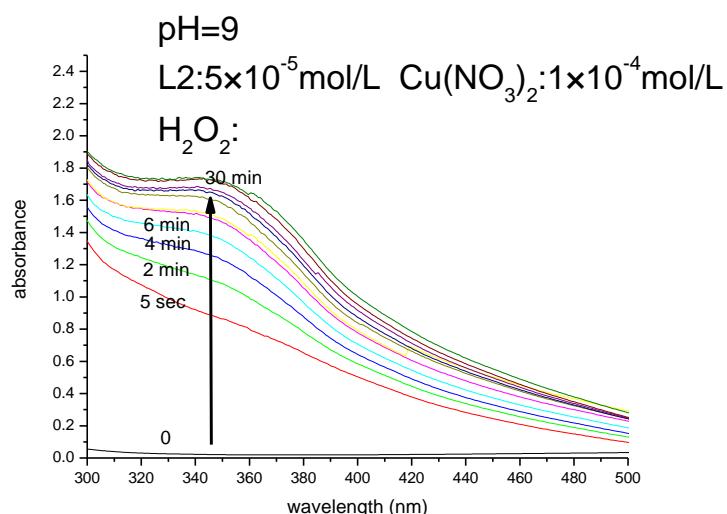


Fig. s12 UV-vis spectra changes after adding 10 μL H₂O₂ to 3.0 ml 2.50×10^{-5} M Cu₂-Lb complex at pH 9.0 aqueous solution

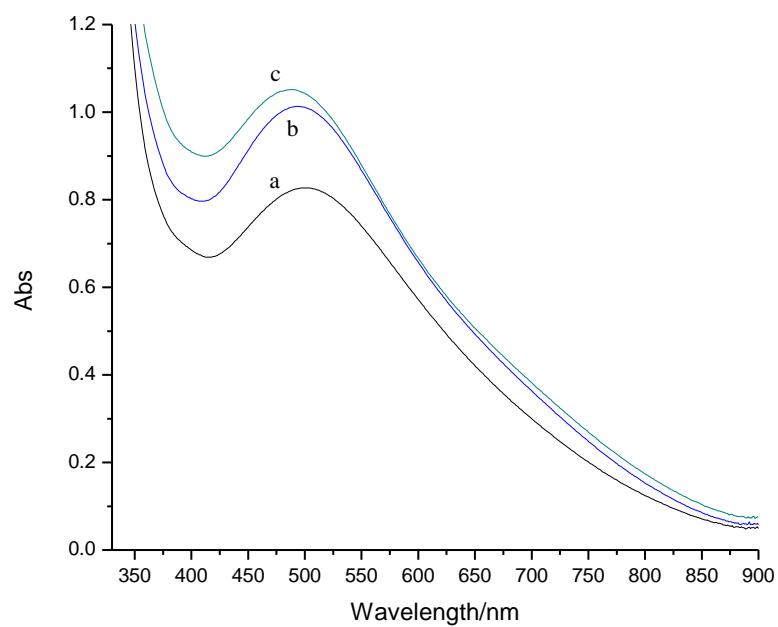


Fig.s13 Spectra of 3.0 ml test solution contains 2.5×10^{-4} M dinuclear copper(II) complex 1.0 ml (pH=8.00), 1.5×10^{-3} M FeSO₄ 1.0mL, 2.0×10^{-2} M sodium salicylate 0.30 mL, and 6.0×10^{-3} M H₂O₂ 0.7ml. The spectra were measured after 30 min (a) No L-2Cu(water instead), (b) Lb-2Cu, (c) Lc-2Cu.

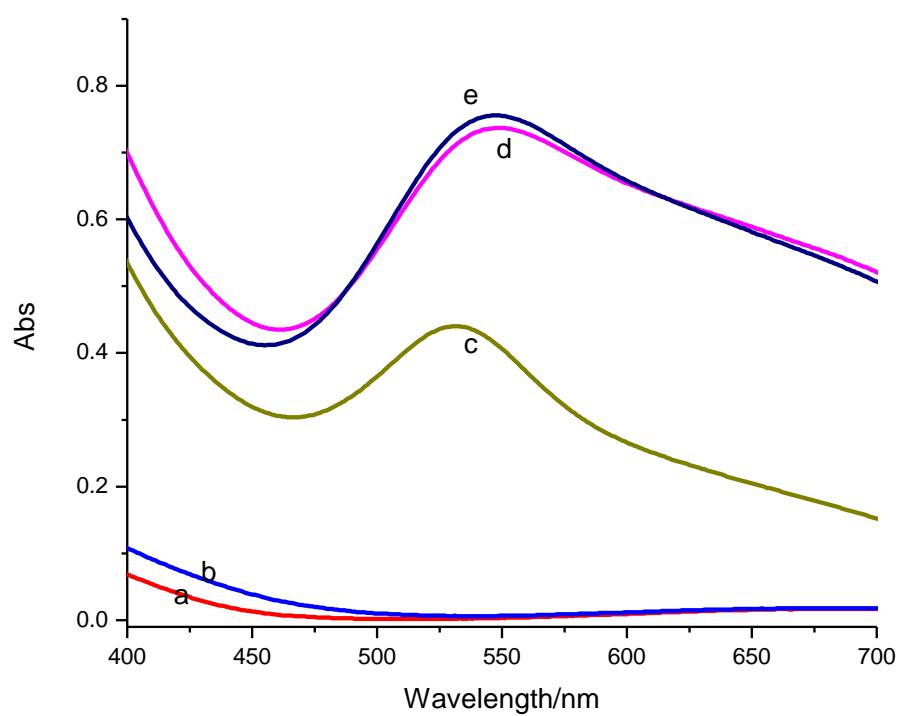


Fig. s14 UV-vis spectra of 1.0×10^{-4} M DPPH, 1.67×10^{-4} M L_c-2Cu complexes, and 1.33×10^{-2} M H₂O₂ system. Test solution is water/methanol (2:1) mixture. (a): L_b-2Cu. (pH 8.0) only. (b): L_c-2Cu (pH 8.0) only. (c): DPPH, L_c-2Cu. (d) DPPH, L_b-2Cu. (e) DPPH only.

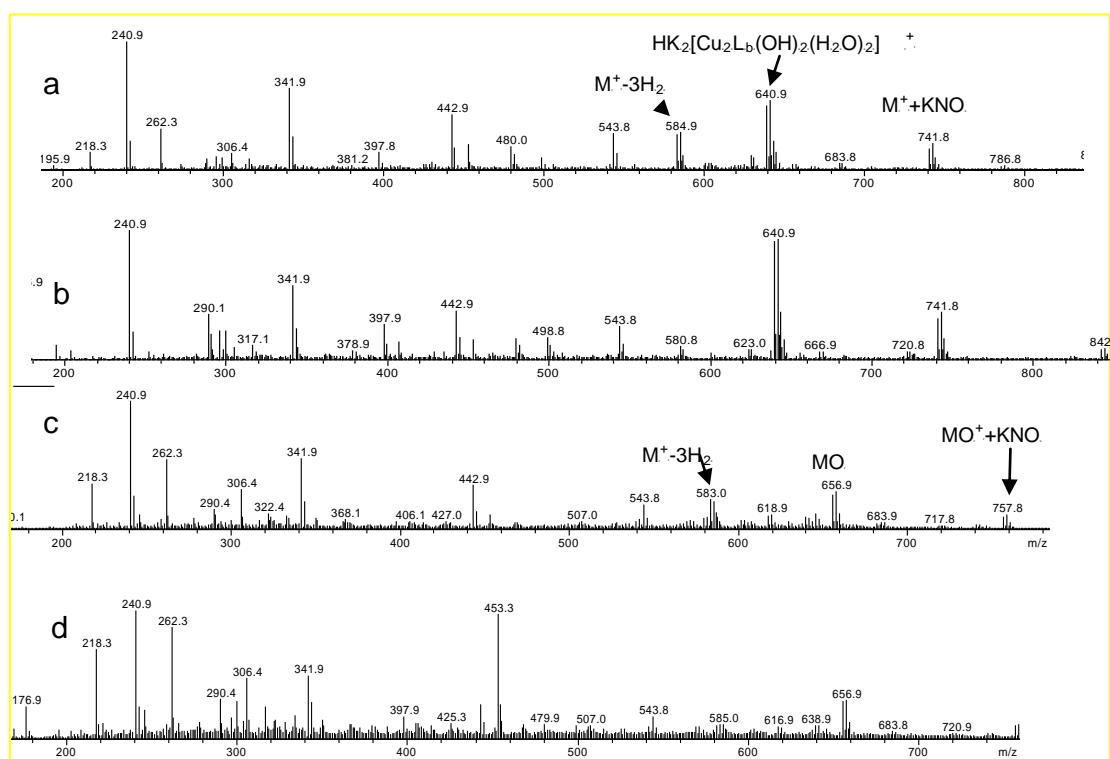


Fig. s15 $\text{L}_b\text{-}2\text{Cu}$ positive mass spectrum (a), pH 7. (b), pH 9. (c), pH7-H₂O₂. (d), pH 9-H₂O₂

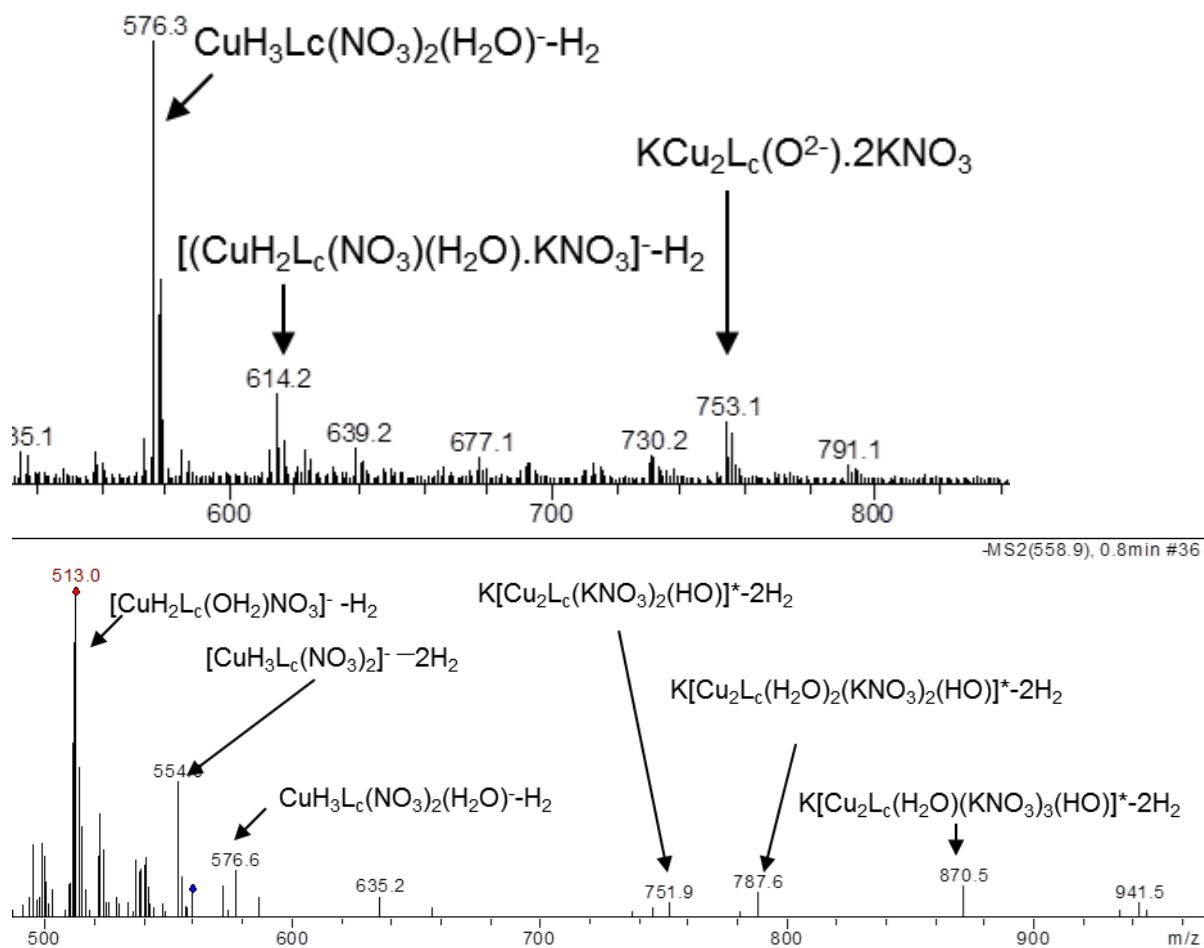


Fig. s16 $\text{L}_\text{c}-2\text{Cu}$ negative ion mass spectrum before (top) and after (bottom) adding H_2O_2 at pH

8.

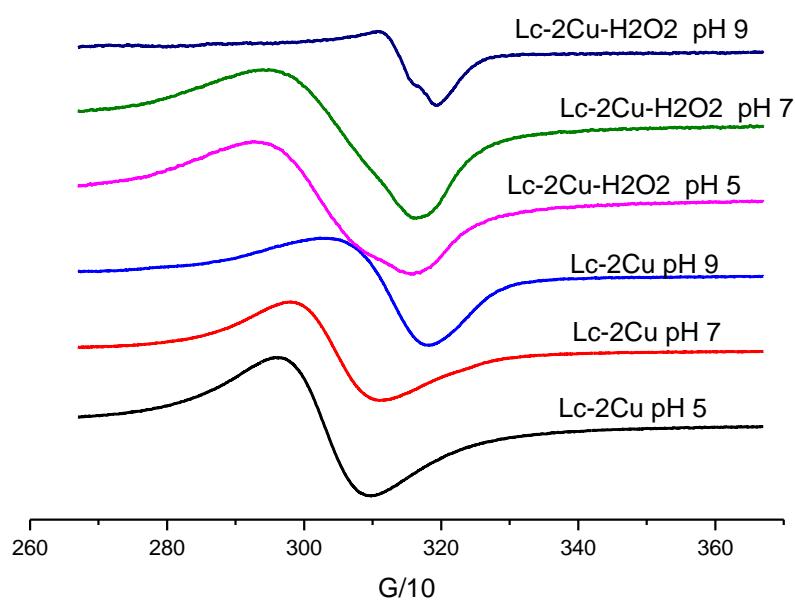
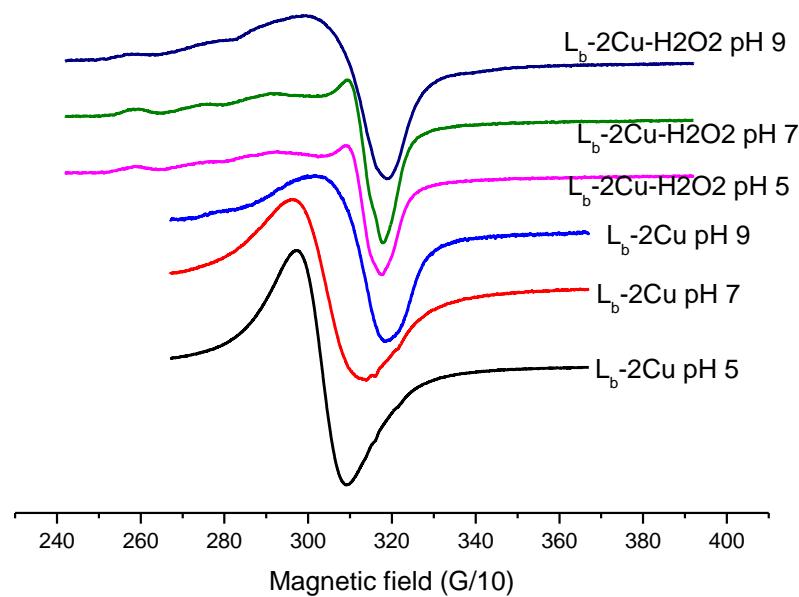


Fig. s17 X-band EPR spectra of 2.5×10^{-3} M copper(II) complex in the absence and presence of 80 equivalent H₂O₂ at different pH at -60 °C. (top: Lb-2Cu complex; bottom: Lc-2Cu complex)

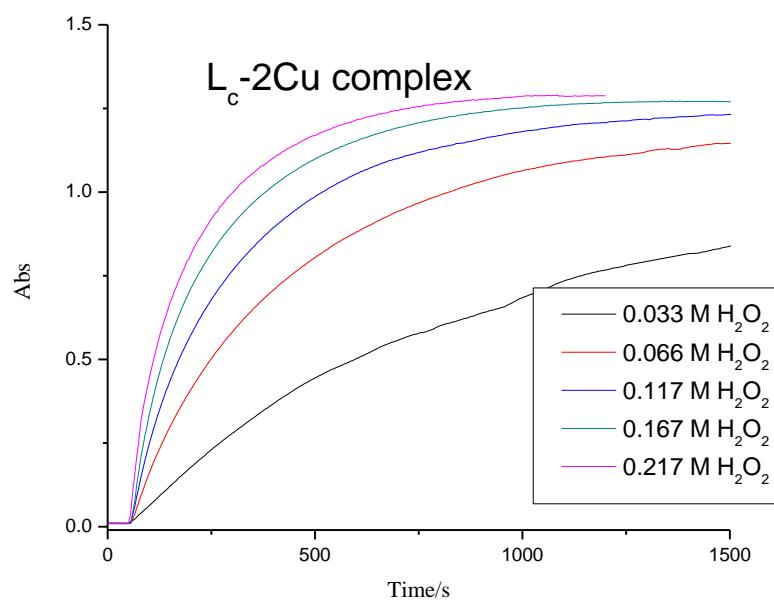
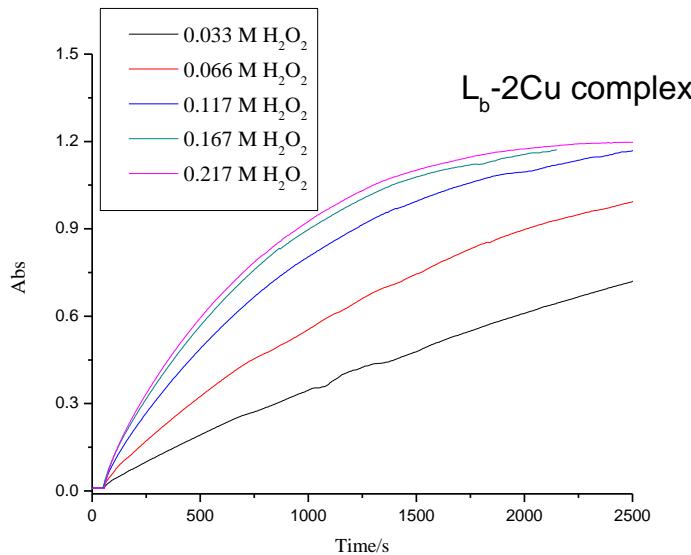


Fig s18 Kinetic traces recorded at 400 nm for the catalyzed degradation of Nitrobenzene.
Reaction conditions: pH=8.00, 0.2 M KH_2PO_4 -NaOH, 1.47×10^{-3} M Nitrobenzene , 3.75×10^{-5} M
 L -2Cu, 25°C, (—) 0.033 M H_2O_2 , (—) 0.066 M H_2O_2 , (—) 0.117 M H_2O_2 , (—) 0.167 M
 H_2O_2 , (—) 0.217 M H_2O_2 .

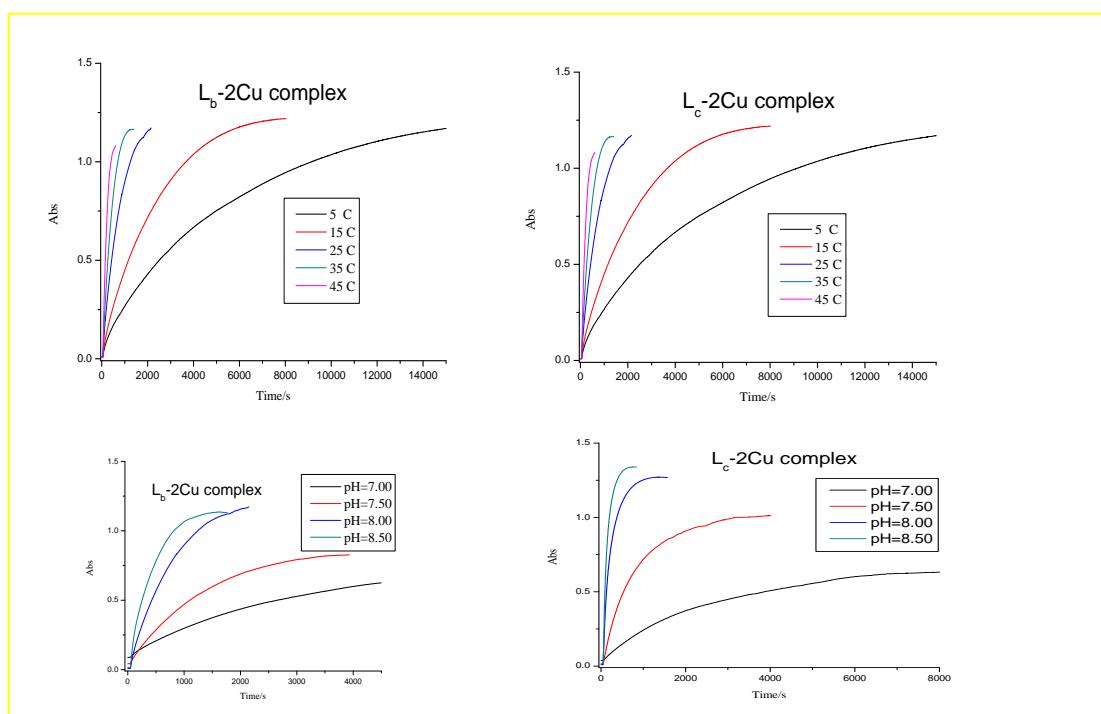


Fig s19 Kinetic traces recorded at 400 nm for the catalyzed oxidation of Nitrobenzene at different temperature and pHs. Reaction conditions: pH=8.00, 0.2 M KH_2PO_4 -NaOH, 1.47×10^{-3} M Nitrobenzene , 3.75×10^{-5} M L -2Cu, 0.167 M H_2O_2 ,

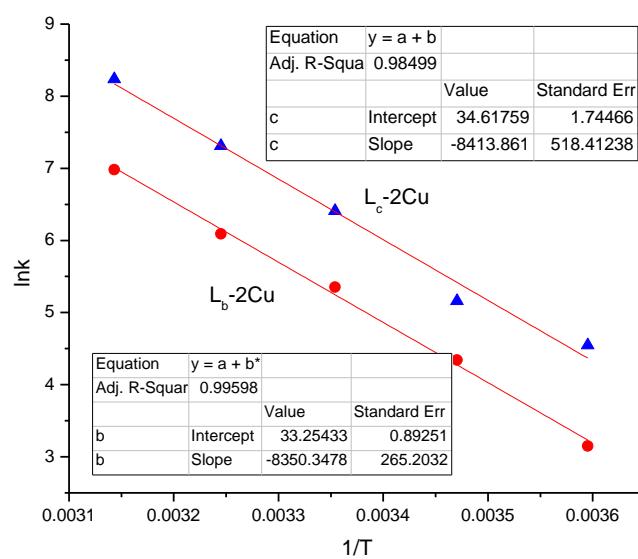


Fig. s20 Plots of $\ln k$ vs $1/T$ for L_b and L_c -2Cu complexes

Table s1. First-order rate constant (s^{-1}) for $1.47 \times 10^{-3} M$ Nitrobenzene and $0.1667 M H_2O_2$ system in different L_b -2Cu concentrations (pH=8.00, 0.2 M phosphate buffer at 25C)

$[L_b\text{-}2\text{Cu}]$	5.00×10^{-6}	1.25×10^{-5}	2.50×10^{-5}	3.75×10^{-5}	5.00×10^{-5}	0
R-Square	0.9962	0.99793	0.99911	0.99911	0.99742	0.99954
k	2.25413E-4	4.56156E-4	8.73259E-4	0.00132	0.00169	6.22797E-5

Table s2. First-order rate constant (s^{-1}) for $1.47 \times 10^{-3} M$ Nitrobenzene and $0.1667 M H_2O_2$ system in different L_c -2Cu concentrations (pH=8.00, 0.2 M phosphate buffer at 25C)

$[L_c\text{-}2\text{Cu}]$	5.00×10^{-6}	1.25×10^{-5}	2.50×10^{-5}	3.75×10^{-5}	5.00×10^{-5}	0
R-Square	0.99924	0.99853	0.99866	0.9984	0.99665	0.99954
k	4.21378E-4	0.00113	0.00269	0.0038	0.0050	6.22797E-5

Table s3. First-order rate constant (s^{-1}) for $1.47 \times 10^{-3} M$ Nitrobenzene and $3.75 \times 10^{-5} M L_b$ -2Cu system in different H_2O_2 concentrations (pH=8.00, 0.2 M phosphate buffer at 25C)

$[H_2O_2]$	0.033	0.066	0.117	0.167	0.217
R-Square	0.99764	0.99843	0.99866	0.99911	0.99673
k	3.1835E-4	5.65061E-4	9.02423E-4	0.00132	0.00172

Table s4. First-order rate constant (s^{-1}) for $1.47 \times 10^{-3} M$ Nitrobenzene and $3.75 \times 10^{-5} M L_c$ -2Cu system in different H_2O_2 concentrations (pH=8.00, 0.2 M phosphate buffer at 25C)

$[H_2O_2]$	0.033	0.066	0.117	0.167	0.217
R-Square	0.99911	0.993	0.99741	0.9984	0.99556
k	6.93459E-4	0.00177	0.00278	0.0038	0.00486