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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Synthetic procedure of the ligands

Scheme s1. Synthetic procedure of ligand L₆
Scheme s2. Synthetic procedure of ligand Lc
Fig. s1. IR spectra of ligand Lb and Lc (KBr disc)

Fig. s2. $^1$H NMR of Lb in D$_2$O
Fig. s3. $^1$H NMR of Lc in D$_2$O

Fig. s4. $^{13}$C NMR of Lc in D$_2$O
MS1:

\[
\text{HOOC} \quad \text{NH} \quad \text{COOH} \quad \text{HN} \quad \text{COOH}
\]

Exact Mass: 374.17

\[
[M+H]^{+} \quad 375.1762
\]

Fig. s5   EI-MS spectra of of Lc in aqueous solution
MS2:

MS3:

MS4:

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 Zn(NO_3)_2 in aqueous solution at 25°C, I=0.10 M KNO_3. top: L_4; bottom: L_c
Fig. 8  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. 9  Spectral changes recorded for the reaction of 5.0×10⁻³ M L₅₂Cu (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 $5.0 \times 10^{-4}$ M L-2Cu with different concentration $\text{H}_2\text{O}_2$ in 0.02 M $\text{KH}_2\text{PO}_4$-$\text{NaOH}$ buffer solution at 25°C, pH=7.50. Top: Lb-2Cu complex; Bottom: Lc-2Cu complex.
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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 L_c-2Cu complexes
**Fig. S12** UV-vis spectra changes after adding 10 μL H$_2$O$_2$ to 3.0 ml 2.50×10$^{-5}$ M Cu$_2$-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 FeSO$_4$ 1.0mL, 2.0×10$^{-2}$ M sodium salicylate 0.30 mL, and 6.0×10$^{-3}$ M H$_2$O$_2$ 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 $1.0 \times 10^{-4}$ M DPPH, $1.67 \times 10^{-4}$ M L-2Cu complexes, and $1.33 \times 10^{-2}$
H$_2$O$_2$ 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  \( \text{L}_\text{d}_{\text{p}}\text{-Cu positive mass spectrum (a), pH 7. (b), pH 9. (c), pH7-H}_2\text{O}_2. \text{ (d), pH 9-H}_2\text{O}_2 \)
Fig. s16  L₂-2Cu negative ion mass spectrum before (top) and after (bottom) adding H₂O₂ 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$_2$PO$_4$-NaOH, 1.47×10$^{-5}$ M Nitrobenzene, 3.75×10$^{-5}$ M L-2Cu, 25°C, (  ) 0.033 M H$_2$O$_2$, (—) 0.066 M H$_2$O$_2$, (——) 0.117 M H$_2$O$_2$, (——) 0.167 M H$_2$O$_2$, (——) 0.217 M H$_2$O$_2$. 

H$_2$O$_2$, (——) 0.217 M H$_2$O$_2$. 

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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 KH2PO4-NaOH, $1.47 \times 10^{-3}$ M Nitrobenzene, $3.75 \times 10^{-5}$ M L-2Cu, 0.167 M H2O2.

Fig. s20  Plots of lnk vs 1/T for L_b and L_c-2Cu complexes
Table s1. First-order rate constant (s⁻¹) for 1.47×10⁻³ M Nitrobenzene and 0.1667 M H₂O₂ system in different L₉-2Cu concentrations (pH=8.00, 0.2 M phosphate buffer at 25°C)

<table>
<thead>
<tr>
<th>[L₉-2Cu]</th>
<th>5.00×10⁻⁶</th>
<th>1.25×10⁻⁵</th>
<th>2.50×10⁻⁵</th>
<th>3.75×10⁻⁵</th>
<th>5.00×10⁻⁵</th>
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<td>R-Square</td>
<td>0.9962</td>
<td>0.99793</td>
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<td>0.99911</td>
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<tr>
<td>k</td>
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<td>0.00132</td>
<td>0.00169</td>
<td>6.22797E-5</td>
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</tbody>
</table>

Table s2. First-order rate constant (s⁻¹) for 1.47×10⁻³ M Nitrobenzene and 0.1667 M H₂O₂ system in different L₉-2Cu concentrations (pH=8.00, 0.2 M phosphate buffer at 25°C)

<table>
<thead>
<tr>
<th>[L₉-2Cu]</th>
<th>5.00×10⁻⁶</th>
<th>1.25×10⁻⁵</th>
<th>2.50×10⁻⁵</th>
<th>3.75×10⁻⁵</th>
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<tr>
<td>R-Square</td>
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Table s3. First-order rate constant (s⁻¹) for 1.47×10⁻³ M Nitrobenzene and 3.75×10⁻⁵ M L₉-2Cu system in different H₂O₂ concentrations (pH=8.00, 0.2 M phosphate buffer at 25°C)

<table>
<thead>
<tr>
<th>[H₂O₂]</th>
<th>0.033</th>
<th>0.066</th>
<th>0.117</th>
<th>0.167</th>
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<td>0.00132</td>
<td>0.00172</td>
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</tbody>
</table>

Table s4. First-order rate constant (s⁻¹) for 1.47×10⁻³ M Nitrobenzene and 3.75×10⁻⁵ M L₉-2Cu system in different H₂O₂ concentrations (pH=8.00, 0.2 M phosphate buffer at 25°C)

<table>
<thead>
<tr>
<th>[H₂O₂]</th>
<th>0.033</th>
<th>0.066</th>
<th>0.117</th>
<th>0.167</th>
<th>0.217</th>
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