

Supporting Information

For

H₂O₂-Reactivity of Copper(II) Complexes Supported by TPA Ligands with 6-Phenyl Substituents.

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Figure S1

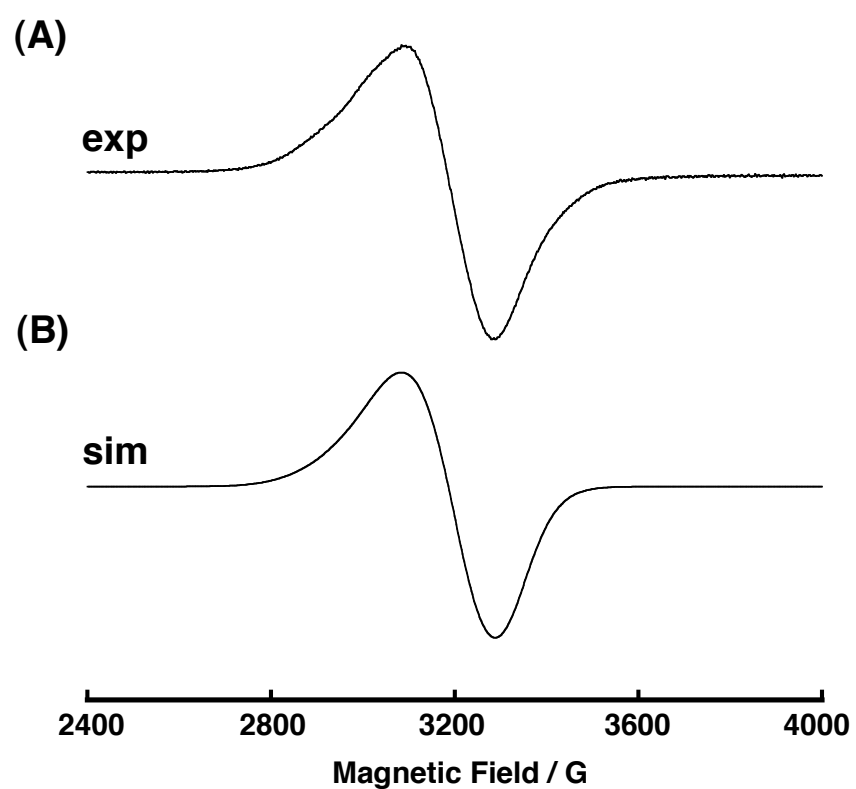


Figure S1. (A) ESR spectrum of **CuTPA** in CH_3CN at $-145\text{ }^\circ\text{C}$ and (B) a computer simulation spectrum with ESR parameters, $g_1 = 2.170$, $g_2 = 2.068$, $g_3 = 2.145$, $A_1 = 100\text{ G}$, $A_2 = 30\text{ G}$, $A_3 = 30\text{ G}$, $W_1 = 200\text{ G}$, $W_2 = 100\text{ G}$, $W_3 = 130\text{ G}$.

Figure S2

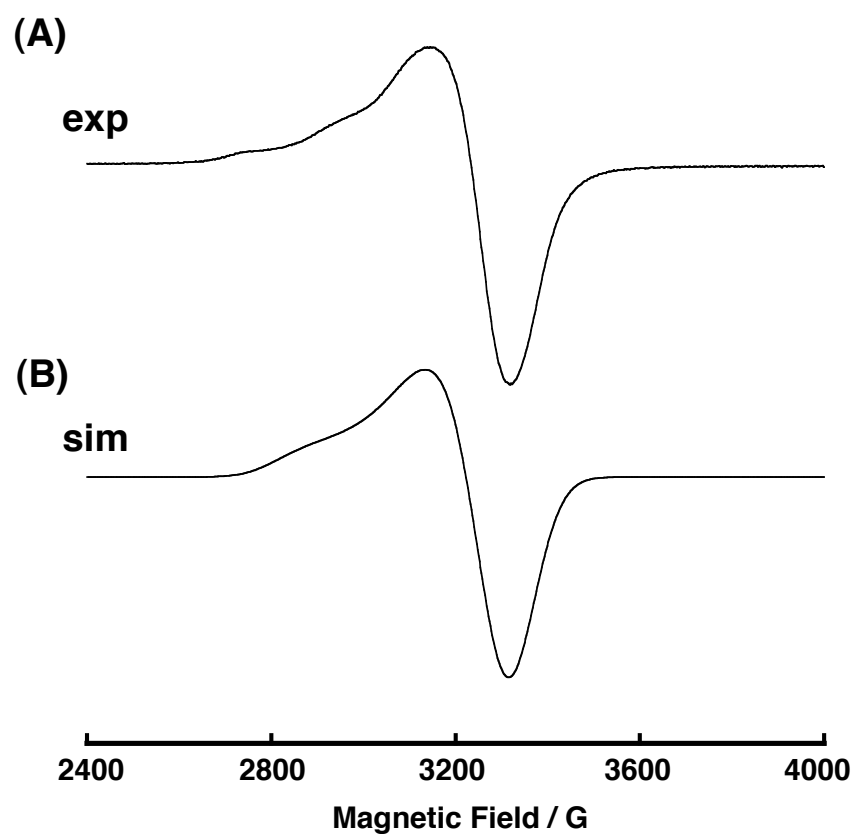


Figure S2. (A) ESR spectrum of **1** in CH₃CN at -145 °C and (B) a computer simulation spectrum with ESR parameters, $g_1 = 2.235$, $g_2 = 2.043$, $g_3 = 2.090$, $A_1 = 100$ G, $A_2 = 5$ G, $A_3 = 30$ G, $W_1 = 130$ G, $W_2 = 110$ G, $W_3 = 150$ G.

Figure S3

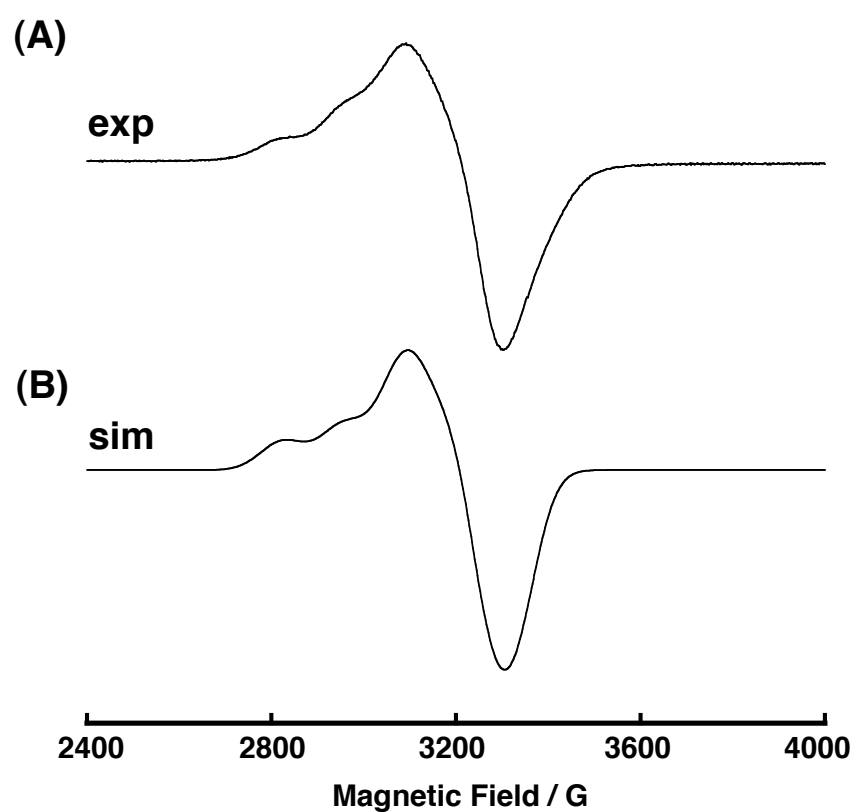


Figure S3. (A) ESR spectrum of **2** in CH₃CN at -145 °C and (B) a computer simulation spectrum with ESR parameters, $g_1 = 2.230$, $g_2 = 2.040$, $g_3 = 2.140$, $A_1 = 130$ G, $A_2 = 18$ G, $A_3 = 18$ G, $W_1 = 96$ G, $W_2 = 90$ G, $W_3 = 100$ G

Figure S4

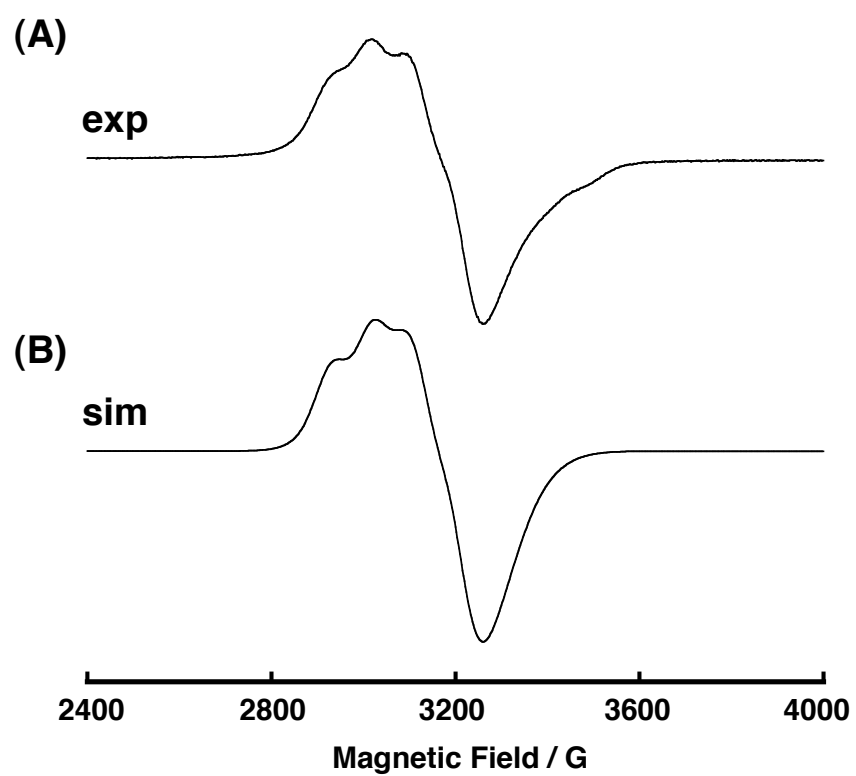


Figure S4. (A) ESR spectrum of **3** in CH₃CN at -144 °C and (B) a computer simulation spectrum with ESR parameters, $g_1 = 2.185$, $g_2 = 2.110$, $g_3 = 2.120$, $A_1 = 90$ G, $A_2 = 2$ G, $A_3 = 22$ G, $W_1 = 58$ G, $W_2 = 160$ G, $W_3 = 230$ G

Figure S5

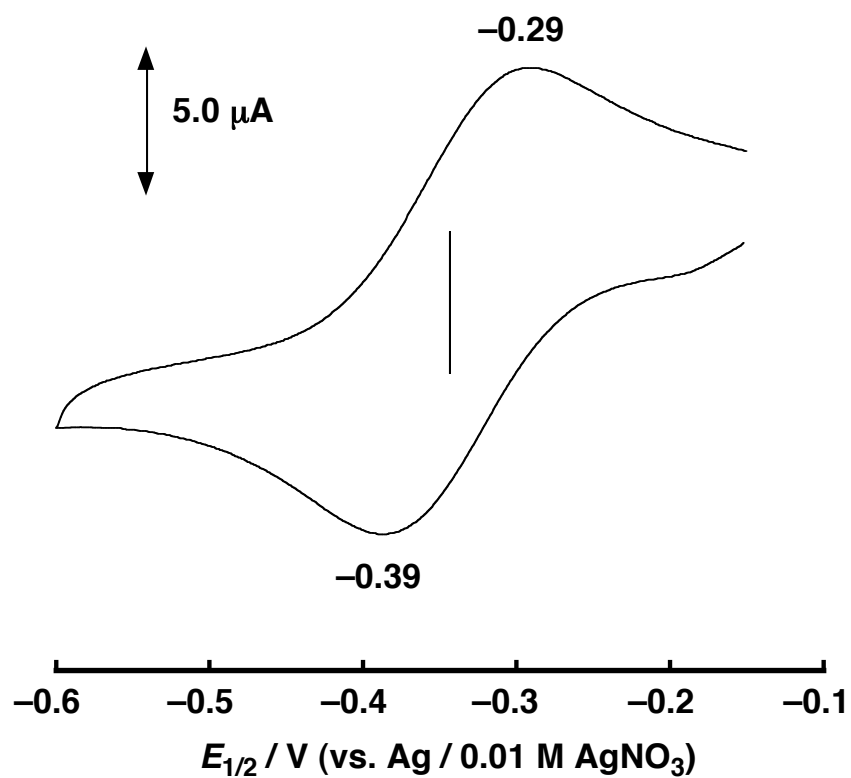


Figure S5. Cyclic voltammogram of **CuTPA** (2.0×10^{-3} M) in CH_3CN containing 0.1 M TBAP; working electrode Pt, counter electrode Pt, pseudo-reference electrode Ag / 0.01 M AgNO_3 , scan rate 50 mV/s.

Figure S6

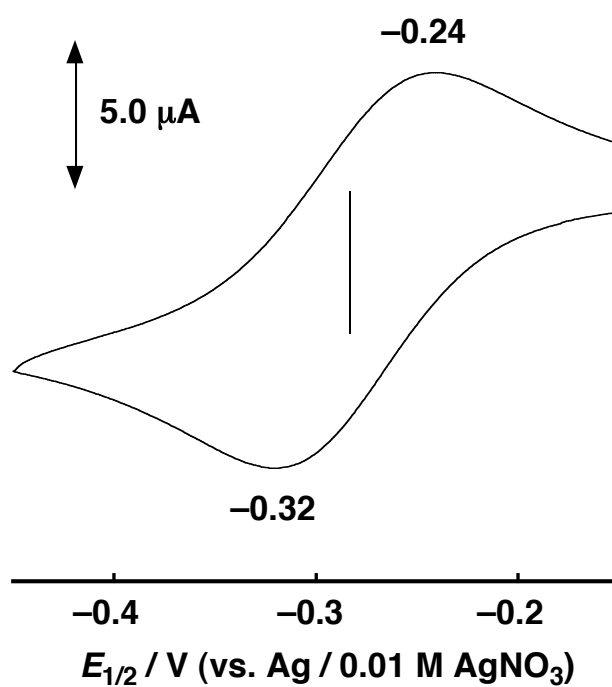


Figure S6. Cyclic voltammogram of **1** (2.0×10^{-3} M) in CH₃CN containing 0.1 M TBAP; working electrode Pt, counter electrode Pt, pseudo-reference electrode Ag / 0.01 M AgNO₃, scan rate 50 mV/s.

Figure S7

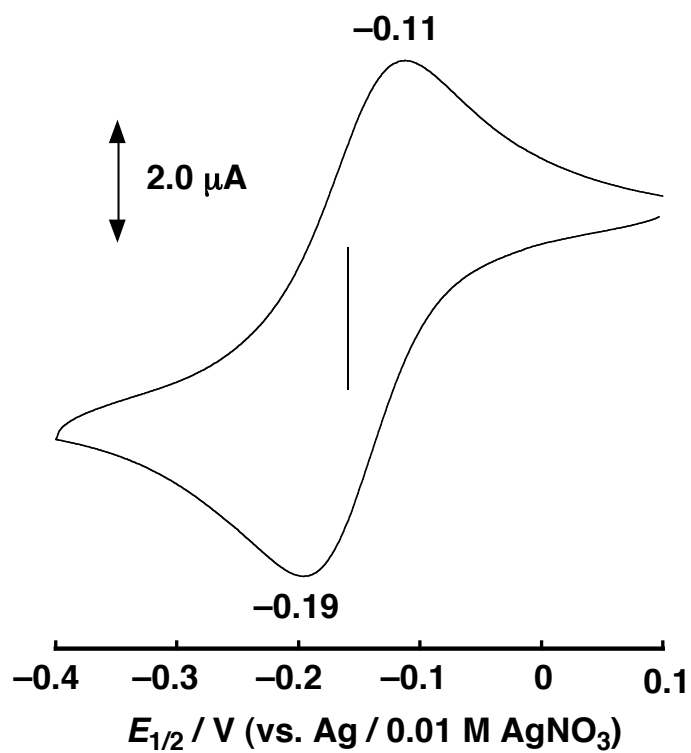


Figure S7. Cyclic voltammogram of **2** ($2.0 \times 10^{-3} \text{ M}$) in CH_3CN containing 0.1 M TBAP; working electrode Pt, counter electrode Pt, pseudo-reference electrode Ag / 0.01 M AgNO_3 , scan rate 50 mV/s .

Figure S8

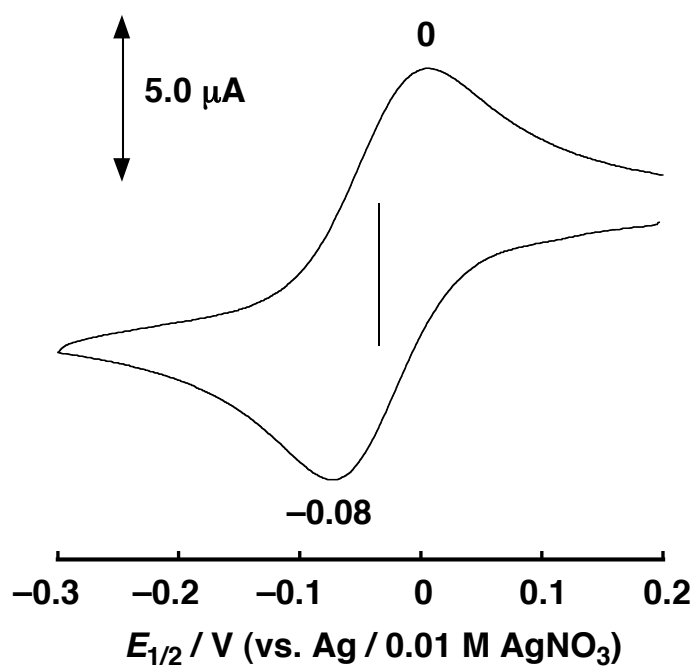


Figure S8. Cyclic voltammogram of **3** (2.0×10^{-3} M) in CH_3CN containing 0.1 M TBAP; working electrode Pt, counter electrode Pt, pseudo-reference electrode Ag / 0.01 M AgNO_3 , scan rate 50 mV/s.

Figure S9

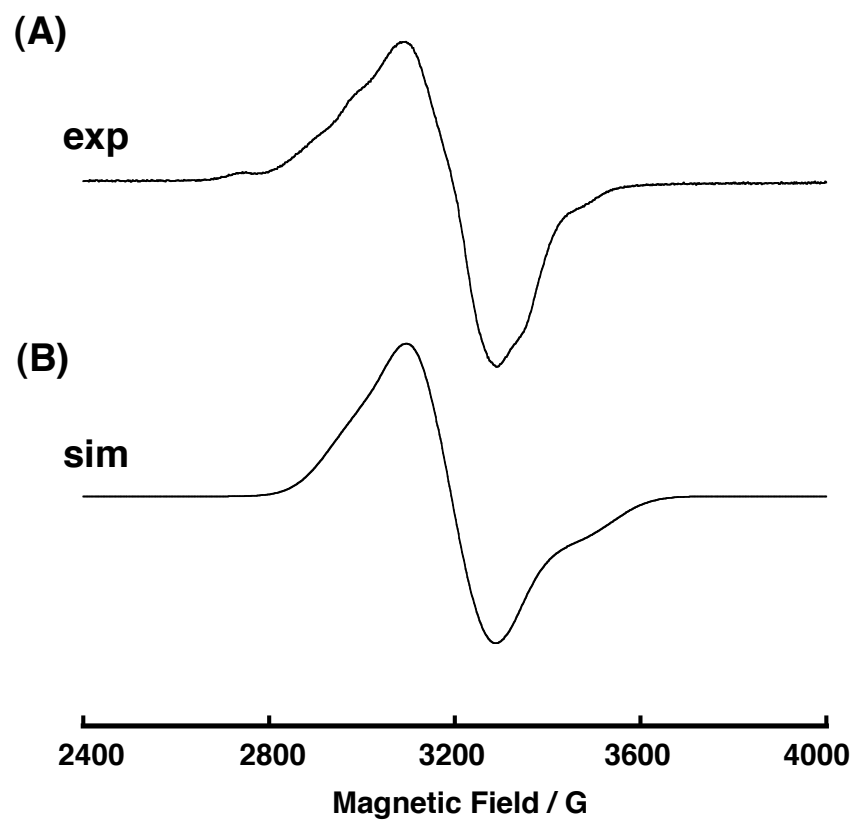


Figure S9. ESR spectrum (A) **1-OOH** in CH₃CN at -144 °C and (B) the computer simulation spectrum with the parameter $g_1 = 2.075$, $g_2 = 2.145$, $g_3 = 2.065$, $A_1 = 166$ G, $A_2 = 20$ G, and $A_3 = 15$ G $W_1 = 150$ G, $W_2 = 100$ G, $W_3 = 95$ G

Figure S10

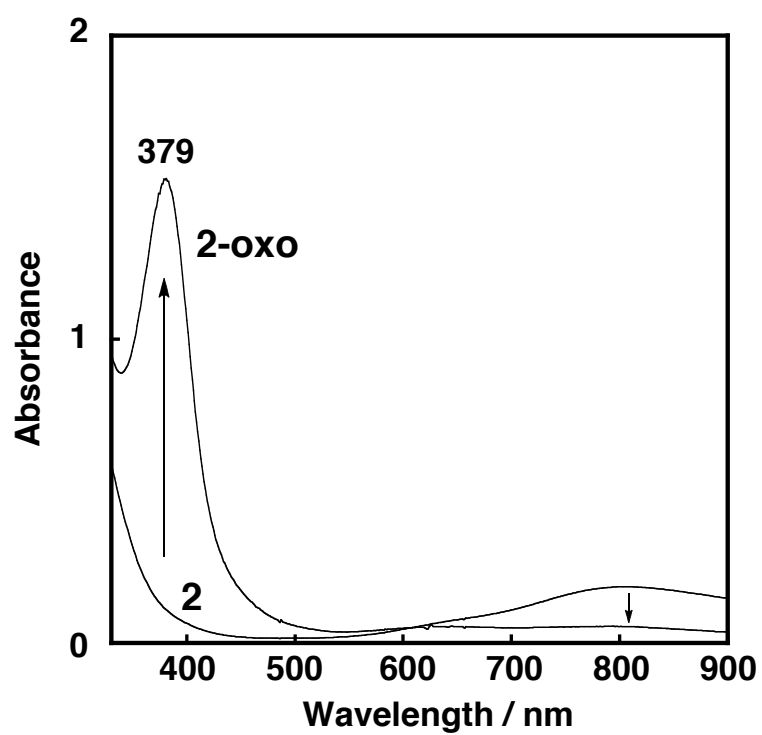
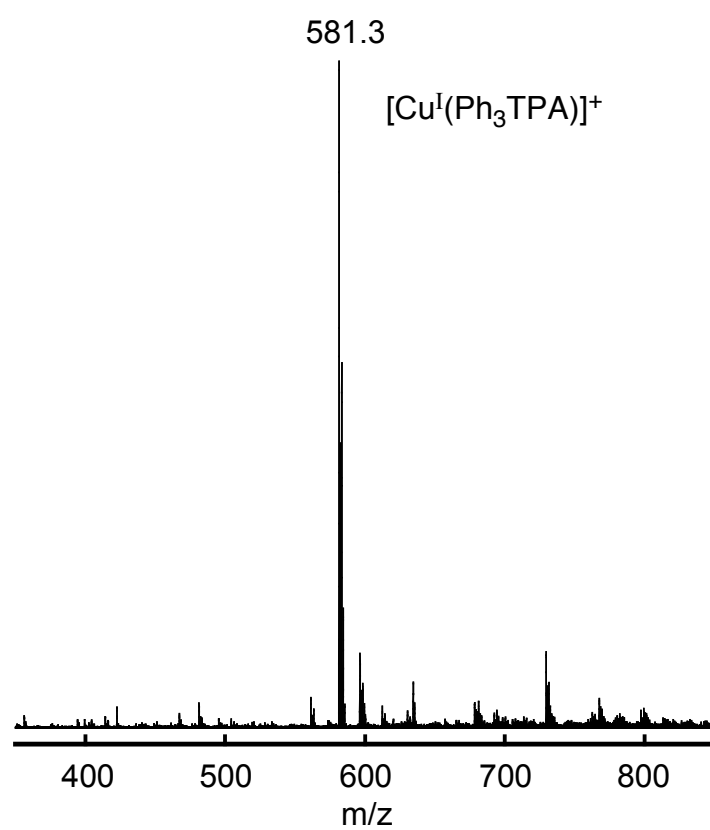


Figure S10. Spectral change for the reaction of **2** (0.6 mM) with H₂O₂ (6.0 mM) in the presence of NEt₃ (1.2 mM) in CH₃CN at -40°C.

Figure S11



Anal. Calcd for $\mathbf{3}^{\text{red}} \cdot 0.5 \text{H}_2\text{O}$ ($\text{C}_{36}\text{H}_{31}\text{Cu}_1\text{Cl}_1\text{N}_4\text{O}_{4.5}$): C, 62.61; H, 4.52; N, 8.11

Found: C, 62.64; H, 4.36; N, 8.09

Figure S11. ESI-MS of $\mathbf{3}^{\text{red}}$ generated by the reaction of **3** and H_2O_2 in CH_3CN and elemental analysis data of $\mathbf{3}^{\text{red}}$.