Supporting Information

For

Formally Copper(III)-alkylperoxo complexes as models of possible intermediates in monooxygenase enzymes

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Experimental Details

Materials and Methods

Preparation and handling of the air-sensitive compounds were carried out under a dinitrogen atmosphere either in a glovebox or using standard Schlenk techniques. All reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. Tetrahydrofuran (THF) was dried over sodium/benzophenone and vacuum distilled. Diethyl ether and pentane was passed through solvent purification columns (Glass Contour, Laguna, California). All solvents were stored over 3 Å molecular sieves in a N_2 filled glove-box prior to use. The compounds (H_2L, L = N,N'-Bis(2,6-diisoproylphenyl)-2,6-pyridinedicarboxamido),[1] [NBu_4][**1**],[2] ferroncenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ([Fc][$B(Ar^F)_4$]),[3] 4-dimethylamino-phenol (^{NMe2}PhOH),[4] and 1-hydroxy-2,2,6,6-tetramethyl-piperidine (TEMPO-H)[5] were synthesized by known published procedures. The compound ([NEt_4][$LCu^{II}OH$], [NEt_4][**1**]), was prepared using the same procedure as reported for the synthesis of [NBu_4][**1**],[2] except tetraethylammonium hydroxide was used instead of tetrabuytlammonium hydroxide. The 80% cumene hydroperoxide (CmOOH) and 9 M *tert*-butyl-hydroperoxide (*t*BuOOH) in nonane were procured from Sigma Aldrich Chemical Co. ^{18}O-enriched cumene hydroperoxide (~ 60% 18 incorporation by ESI-MS) was synthesized by using cumene and $^{18}O_2$ (procured from ICON isotopes) according to a literature procedure.[6] Decamethylferrocene (Fc*) was procured from Sigma-Aldrich.

UV-vis spectra were collected on a HP8453 (190-1100nm) diode array spectrophotometer. Low-temperature UV-vis experiments were performed using a Unisoku low-temp UV-vis cell holder. EPR data was collected on a Bruker Elexsys E500 spectrophotometer using X-band radiation at 35 dB or 55 dB and 30 K. EPR spectral simulations were performed using EasySpin software (version 4.5.5).[7] Cyclic voltammograms were recorded using an EC Epsilon potentiostat from BASi, a platinum working electrode, and an $AgNO_3$/Ag reference electrode. All cyclic voltammograms were internally referenced using Fc* and then the potentials converted with respect to the standard Fc^+/Fc couple.[8] X-ray diffraction measurements were collected with a Cu Kα radiation and a Bruker D8 Photon II CPAD diffractometer using normal parabolic mirrors as monochromators. Resonance Raman (rR) spectra were collected on an Acton 506 spectrometer using a Princeton Instruments LN/CCD-11100-PB/UBAR detector and ST-1385 controller interfaced with *Winspec* software. The spectra were obtained at 77 K using a backscattering geometry. Excitation at 561 nm was provided by a Cobalt Jive 100 mW laser. Raman shifts were externally referenced to indene and internally referenced to solvent (THF). Spectra were baseline corrected and normalized to solvent using *Origin* (2016) software. Hooke's law was used to determine the force constant (k) and the expected shift upon isotopic labeling:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \;\Rightarrow\; k = \mu(2\pi\nu)^2 \qquad (1)$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad (2)$$

where ν is the stretching frequency (in Hz), μ is the reduced mass (in kg), and m_1 and m_2 are the masses of the atoms involved in the vibration (in kg).[9] The final units of k are N m^{-1}, which are converted to mdyn $Å^{-1}$ by dividing by 100.

Preparation of compounds:

([NBu_4][$LCu^{II}OOCm$], [NBu_4][2a]). To a 25 mL Schleck flask, 200 mg (0.25 mmol) of solid [NBu_4][**1**] was added along with activated 3 Å molecular sieves and placed under Argon atmosphere. To this flask 10 mL of anhydrous THF was added, which resulted in dissolution of the [NBu_4][**1**] to give a blue solution. After stirring the solution for 30 min, it was cooled to -20 °C using a salt/ice bath and 0.1 mL of an 80% solution (5 equiv.) of cumene hydroperoxide was added dropwise resulting in a color change from blue to a dark crimson. After stirring for 15 min., the reaction mixture was syringe-filtered using a 25 mM diameter, 0.2 µm hydrophobic polytetrafluoroethylene (PTFE) syringe filter, into a separate dry, flask to remove all molecular sieve particulate. The solvent was removed from the reaction solution in vacuo while at -20 °C and the resulting crimson oil was subsequently dissolved in minimal anhydrous diethyl ether (Et_2O, ~ 5.0 mL) and triturated with pentane 3x until a more powdery product was obtained. The product was then stirred over 10 mL of anhydrous pentane for 12 hours and filtered using a frit funnel to give a crimson colored solid that was washed with pentane 3x and dried on a vacuum line (160 mg, 68% yield). UV-vis (THF, -80 °C) λ_{max}, nm (ε, M^{-1} cm^{-1}): 552 (380), 698 (130). HR-MS (ESI, MeCN) *m/z*: **2a** Calcd. for $[C_{40}H_{48}CuN_3O_4]^-$ 697.294; found 697.208. Repeated attempts to obtain correct CHN analysis were unsuccessful with consistently low carbon composition in the analyses, which we attribute to incomplete combustion. The compound [NEt_4][**2a**] was prepared specifically for crystallization purposes using the analogous synthetic procedure for compound [NBu_4][**2a**] but using [NEt_4][**1**] as a precursor in lieu of [NBu_4][**1**]. X-ray quality crystals were formed from the crude reaction mixture after being subjected to vacuum over a 12 hour period.

([NBu_4][$LCu^{II}OO$*t*Bu], [NBu_4][2b]). The analogous synthetic method for [NBu_4][**2a**] was used except *tert*-butyl-hydroperoxide in nonane was used to give [NBu_4][**2b**] (190 mg, 81% yield). UV-vis (THF, -80 °C) λ_{max}, nm (ε, M^{-1} cm^{-1}): 551 (450), 694 (135). HR-MS (ESI, MeCN) *m/z*: **2b** Calcd. for $[C_{35}H_{46}CuN_3O_4]^-$ 635.278; found 635.270. Repeated attempts to obtain correct CHN analysis were unsuccessful, which we attribute to incomplete combustion. Compound [NEt_4][**2b**] was prepared specifically for crystallization purposes using the analogous synthetic procedure for compound [NBu_4][**2b**] but using [NEt_4][**1**] as a precursor in lieu of [NBu_4][**1**]. X-ray quality crystals were formed by the slow evaporation of pentane solvent into a concentrated THF solution of [NEt_4][**2b**] in a -20 °C freezer.

([NBu_4][$LCu^{II}OPh^{NMe2}$], [NBu_4][5]). Solid [NBu_4][**1**] (150 mg, 0.186 mmol) and 38 mg (0.279 mmol) of 4-dimethylamino-phenol was mixed along with activated 3 Å molecular sieves in a 20 ml vial inside a N_2 filled dry box. To this mixture 10 mL of anhydrous THF was added, which resulted in the immediate formation of a deep purple solution. After stirring for 30 min. the reaction mixture was syringe-filtered using a 25 mM diameter, 0.2 µm hydrophobic polytetrafluoroethylene (PTFE) syringe filter, into a separate vial to remove all the molecular sieve particulate. The residual pulverized sieves were rinsed with anhydrous THF (3 x 2 mL) to extract all adhered compound and the resulting solution was syringe-filtered analogously and combined with the original filtrate. The combined solution was then concentrated *in vacuo* to ~ 2 mL and to the resulting solution excess diethyl ether (Et_2O, ~ 15 mL) was added and the mixture was stirred vigorously. The fine solid that precipitated out was isolated by filtration on a fine-pore size frit and washed with copious amounts of Et_2O and dried thoroughly to yield a deep

purple colored solid (155 mg, 90 %). UV-vis (THF, -80 °C) λ_{max}, nm (ε, M^{-1} cm^{-1}): 462 (1,000), 533 (1,100), 726 (570). HR-MS (ESI, MeCN) *m/z*: **5** Calcd. for $[C_{39}H_{47}CuN_4O_3]^-$ 682.294; found 682.187.

Electrospray Ionization Mass Spectrometry (ESI-MS) of 2a, 2b, 5 and ^{18}O-labeled 2a. A 1 mL aliquot of a 1 mM THF solution of **2a** or **2b** was injected into a electrospray ionization source and analyzed. Additionally, a Polyethylene Glycol (PEG) standard was injected along with analyte and the corresponding mass/charge signals were corrected based on the known masses of the PEG standard.

For the ^{18}O-labeled **2a** sample only low resolution ESI-MS data was obtained. A 1 mL aliquot of the 2 mM THF solution was injected into an electrospray ionization source and analyzed. Incorporation of ^{18}O in the complex was determined by the relative peak heights of the feature at *m/z* = 697 and *m/z* = 701 using equation 3

$$\%^{18}O\ incorporation = 100\% * \left(\frac{(M_{701b} - M_{701a})}{((M_{701b} - M_{701a}) + M_{697})}\right) \qquad (3)$$

where M_{701b} is the total peak height at *m/z* = 701, M_{701a} is the predicted contribution to the *m/z* = 701 feature due to naturally occurring isotopes of the unlabeled complex and M_{697} is the total peak height of the feature at *m/z* = 697.

Oxidation Reactions. A necked 1 cm UV-vis cuvette in the Unisoku low-temp UV-vis cell holder containing 1.8 mL of THF and a stir bar was cooled to -80 °C. To this cell, 0.1 mL of a 2 mM THF solution of $[NBu_4]$[**2a**], $[NBu_4]$[**2b**], or $[NBu_4]$[**5**] was added. After mixing and allowing for temperature stabilization (5 min), a UV-vis spectrum was recorded. To the stirring mixture, 0.1 mL of a 2 mM solution of $[Fc][B(Ar^F)_4]$ was injected and stirred. The spectrum was immediately recorded upon addition of oxidant. EPR samples were prepared by injecting a 0.15 mL aliquot of a 2 mM THF solution of $[NBu_4]$[**2a**] or $[NBu_4]$[**2b**] to a quartz EPR sample tube and cooling to ~-80 °C using a liquid N_2/acetone bath. To this cooled tube a 0.15 mL aliquot of a 2 mM THF solution of $[Fc][B(Ar^F)_4]$ was added, mixed using the tip of the syringe needle, and then immediately frozen in liquid nitrogen for storage and analysis.

Preparation of resonance Raman samples of $[NBu_4]$[2a]. To a dry schlenk flask with 3 Å mol. sieves, 40.3 mg of $[NBu_4]$[**1**] was added and dissolved in 4.9 mL of anhydrous THF. The blue reaction solution was cooled to -20 °C using a salt/ice bath and 0.1 mL of cumene hydroperoxide in cumene or 18-O enriched cumene hydroperoxide in cumene was added, producing a color change from blue to light crimson. This mixture was allowed to stir for 20 min. and then a 0.15 mL aliquot was injected into a septa covered quartz EPR sample tube under dry N_2 atmosphere and cooled to ~-80 °C using a liquid N_2/acetone bath. To this cooled tube a 0.15 mL aliquot of a 10 mM THF solution of $[Fc][B(Ar^F)_4]$, was added, mixed using the tip of the syringe needle and then immediately frozen in liquid nitrogen for storage and analysis.

Oxidation titration of $[NBu_4]$[2a]. To a cuvette with 1.8 mL of THF and a stir bar in the Unisoku low temperature cell holder at -80 °C was added 0.1 mL of a stock solution of $[NBu_4]$[**2a**] (2 mM). After temperature equilibration (10 min), 0.1 mL of THF solutions $[Fc][B(Ar^F)_4]$ of varying concentration (corresponding to 0.0–2.0 equivalents) were added and the UV-vis spectra were recorded. This was repeated 11 times, where one titration data point corresponds to a single reaction with specific equivalent amount of $[Fc][B(Ar^F)_4]$ (Figure S10).

Reversible oxidation/reduction of [NBu_4][2a]. To a cuvette with 1.8 mL of THF and a stir bar in the Unisoku low temperature cell holder at -80 °C was added 0.1 mL of a stock solution of [NBu_4][**2a**] (2 mM). After temperature equilibration (10 min), 0.1 mL of a 2 mM solution of [Fc][$B(Ar^F)_4$] was injected and stirred and the spectrum immediately recorded. To this oxidized solution, 0.1 mL of a 2 mM solution of Fc* was added and the resulting spectrum recorded. The addition of 0.1 mL of [Fc][$B(Ar^F)_4$] (oxidant) and Fc* (reductant) was repeated with spectra taken after each addition. The UV-vis spectra shown in Figure S11 were corrected for concentration as a function of volume change due to addition of reagents.

Kinetics analysis of the reactions of 3a. A necked 1 cm UV-vis cuvette in the Unisoku low-temp UV-vis cell holder, containing 1.7 mL of THF was cooled to -80 °C or -25 °C respectively. To this cell 0.1 mL of a 2 mM THF solution of [NBu_4][**2a**] was added. Continuous collection of the UV-vis absorption spectrum was initiated as soon as 0.1 mL of a 2 mM solution of [Fc][$B(Ar^F)_4$] was injected to the mixture. Upon observation of the full growth of the oxidized feature of **3a**, 0.1 mL of a solution of the desired substrate was added to the cell. The decay of **3a** was monitored until no changes to the UV-vis spectrum could be detected. The single wavelength kinetic trace was determined by the disappearance of the UV-vis feature due to **3a** at 504 nm. The pseudo first order rate constants, k_{obs}, were determined from the decay of **3a** as a function of time. Second order rate constants for TEMPO-H reactions were approximated by producing a linear fit using the plot of k_{obs} vs. [TEMPO-H] and obtaining the second order rate constant from the slope of the linear fit of this data (Figure S25).

Theoretical Methods. Density Functional Theory (DFT) calculations were performed using the *ORCA* (v.3.0.2) program.[10] Starting geometries for copper-alkylperoxo complexes were based on the respective X-ray crystal structures. Complexes were optimized spin-unrestricted (UKS) using the *m*PWPW functional with a Def2-QZVP basis set on Cu and other atoms set to a Def2-TZVP basis set, the Resolution of Identity (RI) approximation, Def2-TZV/J auxiliary basis set, tight SCF convergence (VeryTightSCF), and a large integration grid (Grid6).[11-13] The *m*PWPW functional was previously shown to give acceptable geometries for copper-oxygen complexes.[14] Numerical frequency calculations on all complexes confirmed stable structures with no imaginary frequencies observed. A comparison of the bond metrics for the DFT optimized structures with the crystal structures is shown in Table S2. To determine the O-O vibration, the generated Hessian file was rerun through the '*orca_vib*' program where the mass of oxygen was changed to 18 amu, as documented in the *ORCA* manual. Large shifts in energy were used to assign the stretching vibration, which was confirmed upon visualization of the highly-coupled vibration, see video in Supporting Information.

Spin density plots for **2a** and **b** were generated from single point calculations using the BP86 functional[15] with the 'Partridge-3' basis set,[16] the RI approximation, and a TZV/J auxiliary basis set, as used previously.[17] Broken-symmetry calculations were computed using the 'Flipspin' command on the Cu atom starting from the singlet or triplet state geometries with the same basis set mentioned above using a range of functionals: *m*PWPW,[11] BP86,[15] OLYP,[18] TPSS,[19] M06-L,[20] B3LYP,[21] PBE0,[22] TPSSh,[23] M06,[24] PW6B95,[25] and M06-2X.[24] Hybrid- and meta-hybrid-GGA functionals additionally used the Resolution of Identity – Chain of Spheres (RIJCOSX) approximation with an elevated COSX integration grid (GridX4).[26] The 'double-hybrid' functional PWPB95[27] was utilized (including the RIJK approximation with Def2-TZVP/JK and Def2-TZVP/C auxiliary basis sets using a frozen core) by running single-point energy calculations on the triplet state optimized geometry and the broken-symmetry solution from the

PBE0 calculation. The singlet-triplet energy gaps were 'spin purified' by the following, equation 4,[28]

$$E_S = E_T - 2\left[\frac{E_T - E_{BS}}{2 - \langle S^2_{BS}\rangle}\right] \quad (4)$$

where E_T, E_S, and E_{BS} are the electronic energies of the triplet, singlet, and broken-symmetry singlet states, respectively, and $\langle S^2_{BS}\rangle$ is the expectation value of the spin operator from the broken-symmetry singlet state. Time-dependent DFT (TD-DFT) calculations were performed with the PBE0 functional, Def2-TZVP basis set, Def2-SVP/J auxiliary basis set, the Zero-Order Regular Approximation (ZORA)[29] for Cu, RIJCOSX, Grid4, TightSCF, and the Tamm-Dancoff approximation[30] for 40 excited states. Surface contour plots were generated using the *Molekel* (v.5.4.0.8) program with isodensity values set to ±0.003 for spin density plots, ±0.002 for TD-DFT difference plots and ±0.02 for Kohn-Sham molecular orbitals.[31] The programs *Avogadro* (v.1.2.0) and *Gabedit* (v.2.4.8) were also utilized.[32,33]

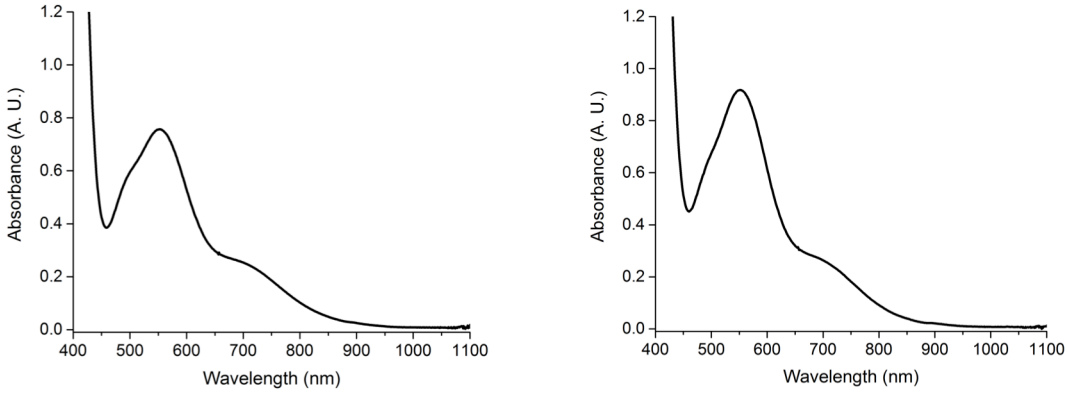

Figure S1. UV-visible spectra of [NBu_4][**2a**] (left) and [NBu_4][**2b**] (right) in THF at -80 °C (2 mM).

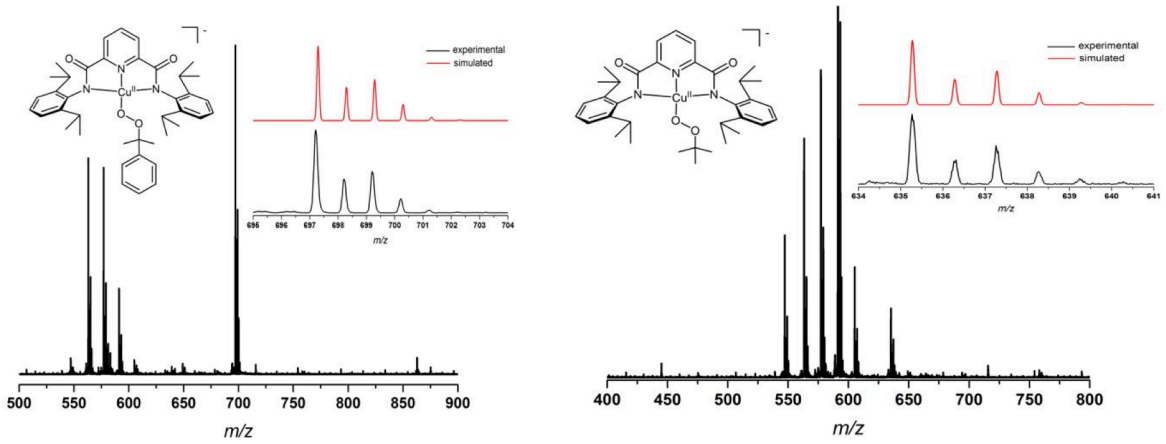

Figure S2. Negative mode high resolution ESI-MS of [NBu_4][**2a**] (left) and [NBu_4][**2b**] (right), with simulated isotopic patterns for the parent ions compared to the experimental data as insets.

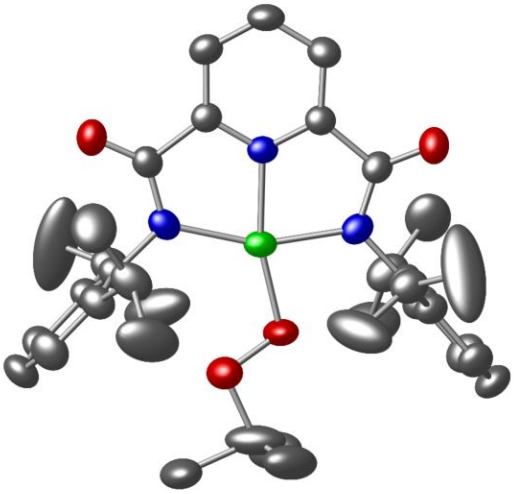

Figure S3. Representation of the X-ray crystal structure of **2b** anion, shown as 50% thermal ellipsoids (H atoms and disordered component of –OOtBu group omitted for clarity). For details, including interatomic distances and angles, see the CIF.

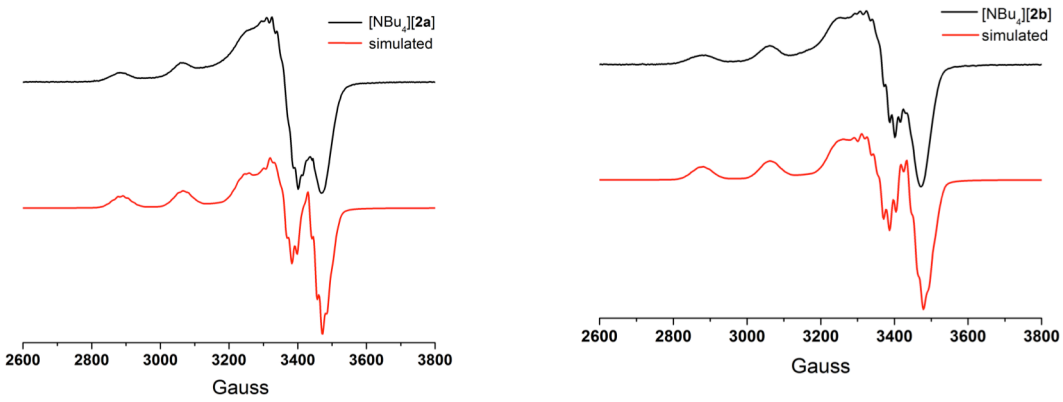

Figure S4. Continuous wave X-band (9.64 GHz) EPR spectra of $[NBu_4][\mathbf{2a}]$ and $[NBu_4][\mathbf{2b}]$ with their respective simulated spectra in THF at 30 K and 35 dB.

Table S1. EPR parameters from spectral simulations.

Compound	$[NBu_4][\mathbf{1}]^2$	$[NBu_4][\mathbf{2a}]$	$[NBu_4][\mathbf{2b}]$
g(x)	2.026	2.044	2.042
g(y)	2.047	2.041	2.042
g(z)	2.194	2.183	2.185
$A^{Cu}(x)$	57	45	60
$A^{Cu}(y)$	57	45	60
$A^{Cu}(z)$	567	535	550
A^{Py} (x)	30	40	55
$A^{Py}(y)$	50	40	55
$A^{Py}(z)$	30	50	50
$A^{am}(x)$	32	45	45
$A^{am}(y)$	50	50	45
$A^{am}(z)$	30	45	45

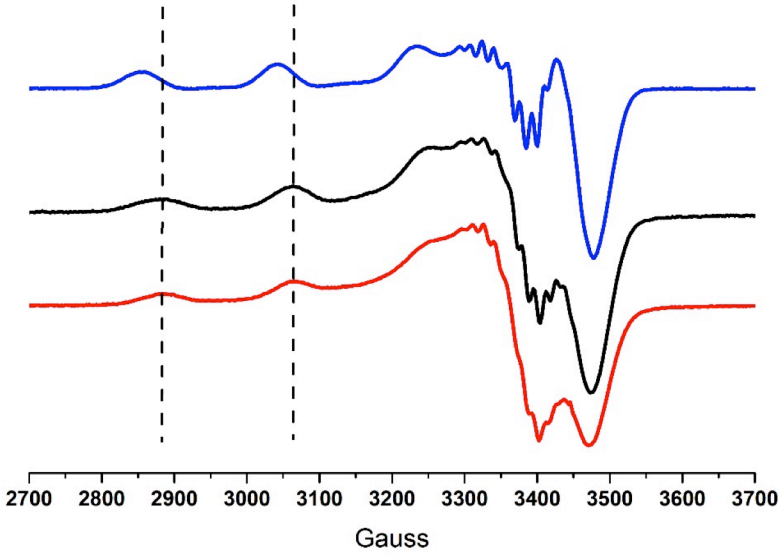

Figure S5. Continuous wave X-band (9.64 GHz) EPR spectra of [NBu_4][**1**] (blue), [NBu_4][**2a**] (black), and [NBu_4][**2b**] (red) in THF at 30 K and 35 dB, with the dashed lines highlighting key spectroscopic differences between [NBu_4][**1**] and the alkylperoxo

Table S2. Geometric parameters compared between XRD data and DFT optimized structures.

	Complex	[**2a**][NEt_4]	[**2a**][NEt_4]	[**2a**]$^-$	**3a**	**3a**	[**2b**][NEt_4]	[**2b**]$^-$	**3b**	**3b**
	Method[a]	XRD	XRD	DFT	DFT (S)	DFT (T)	XRD	DFT	DFT (S)	DFT (T)
Bond Length (Å)	**Cu-O**	1.8410(14)	1.8240(17)	1.881	1.860	1.929	1.855(4)	1.874	1.856	1.923
	Cu-N_{py}	1.9336(15)	1.9303(16)	1.964	1.911	1.961	1.931(2)	1.960	1.908	1.958
	Cu-N_{am}	2.0194(15)	2.0171(15)	2.095	2.006	2.059	2.0073(19)	2.101	1.995	2.058
	Cu-N_{am}	2.0258(15)	2.0260(16)	2.115	1.995	2.053	2.0074(19)	2.110	2.001	2.044
	O-O	1.4689(19)	1.469(2)	1.449	1.407	1.364	1.416(6)	1.449	1.405	1.363
	O-C	1.433(3)	1.414(3)	1.461	1.493	1.523	1.524(6)	1.452	1.482	1.507
Torsion Angle (°)	**N_{am}-Cu-O-O**	22.93(15)	10.6(2)	9	4	80	6.32	5	3	63
	Cu-O-O-C	150.04(14)	169.60(18)	129	127	175	179.61	136	128	178
	τ_4[b]	0.22	0.22	0.29	0.24	0.23	0.25	0.28	0.23	0.23
	BVS[c]	2.2	2.3	1.9	2.5	2.1	2.2	1.9	2.5	2.1

[a] X-ray Diffraction (XRD) structures with estimated standard deviations shown in parentheses where there are two independent molecules in the asymmetric unit for [**2a**][NEt_4], and Density Functional Theory (DFT) structures calculated at the *m*PWPW / Def2-TZVP | Def2-QZVP(Cu) level where (S) is singlet state and (T) is triplet state. [b] τ_4 value where 0 = square planar and 1 = tetrahedral geometries about the copper.[34] [c] Bond Valance Sum (BVS) analysis to approximate

the oxidation state of the copper for structures **2a,b** [B = 0.37; R_0 is 1.679 (Cu^{II}-O) and 1.751 (Cu^{II}-N)] and **3a,b** [B = 0.37; R_0 is 1.735 (Cu^{III}-O) and 1.768 (Cu^{III}-N)].[35]

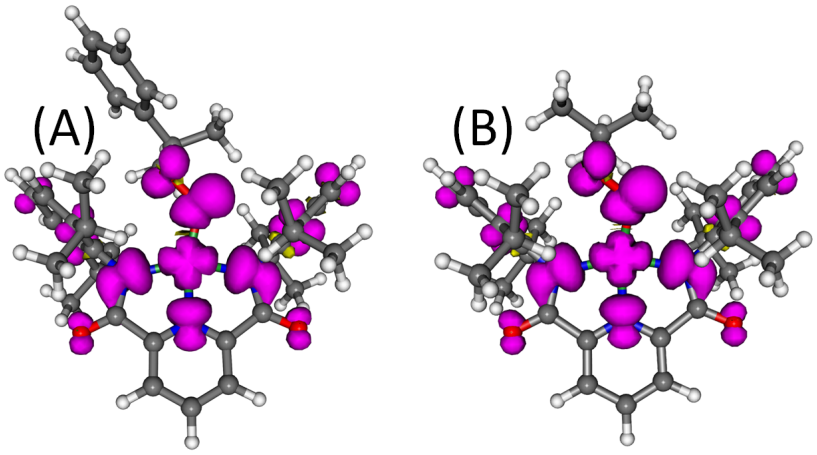

Figure S6. Spin density plots (pink is positive density, yellow is negative density) of $[CuOOR]^+$ for [(A) R = cumyl [**2a**]$^-$; (B) R = tBu [**2b**]$^-$, right) using BP86/Partridge-3 level of theory where gray, white, blue, red, and green atoms represent C, H, N, O, and Cu, respectively.

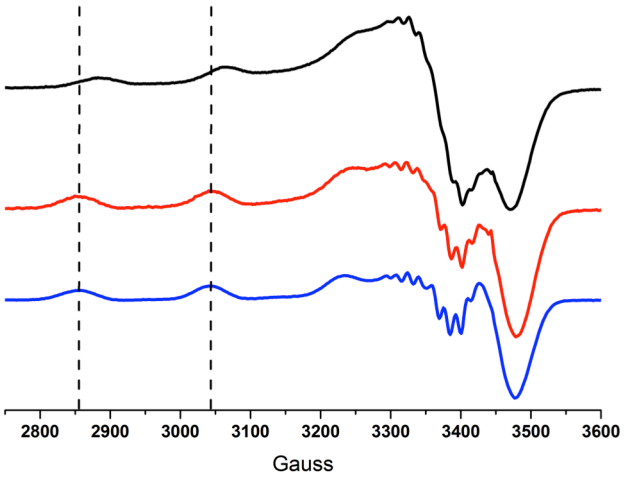

Figure S7. Continuous wave X-band (9.64 GHz) EPR spectra of $[NBu_4]$[**2a**] (black), $[NBu_4]$[**2a**] decay product (red), and $[NBu_4]$[**1**] (blue) in THF at 30 K and 35 dB.

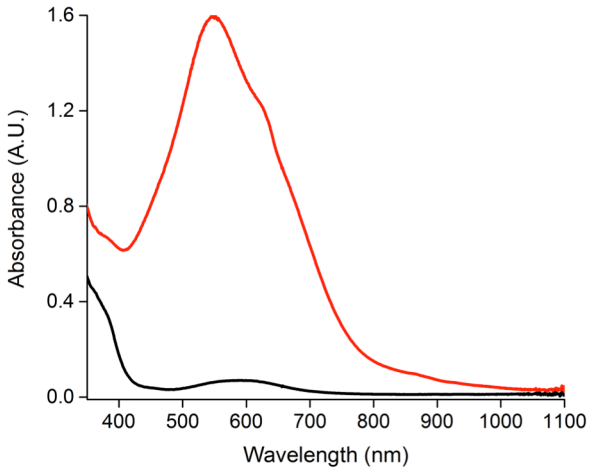

Figure S8. UV-vis spectra of [NBu_4][**2a**] decay product (~0.1 mM) (black), and the product of reaction of that decay product with an equiv. of [Fc][$B(Ar^F)_4$] (red) in THF at -80 °C. This latter spectrum matches that reported previously for LCuOH.

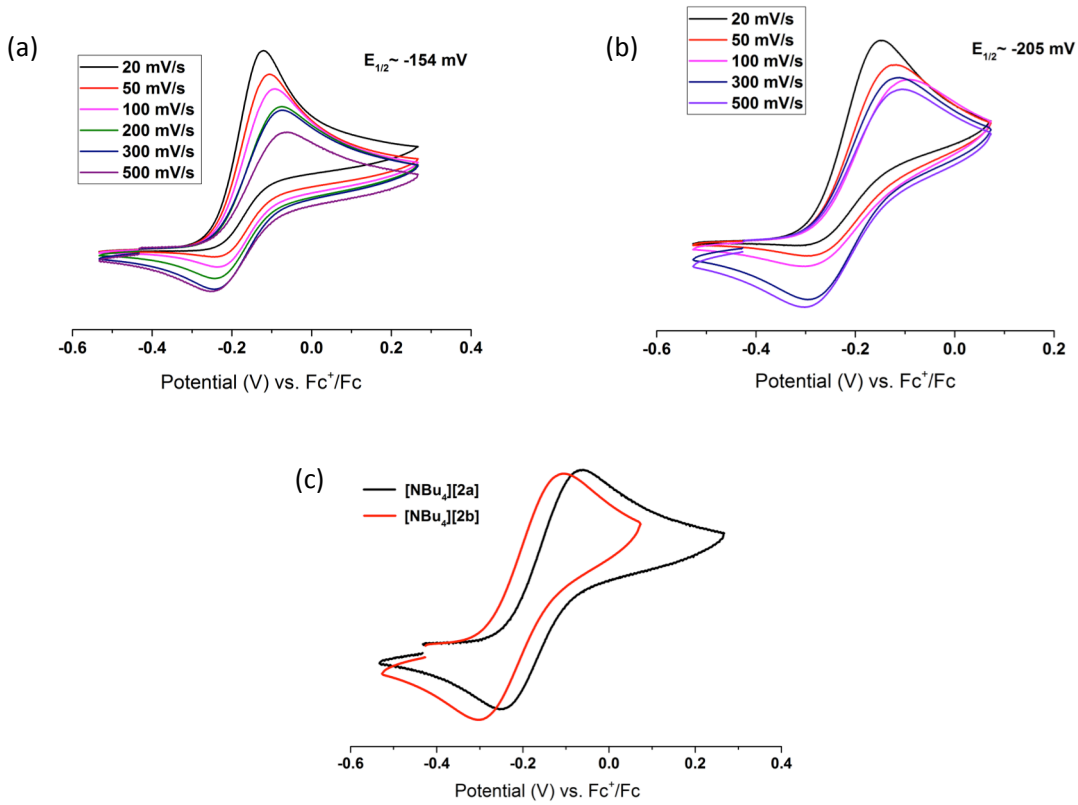

Figure S9. Scan rate normalized (where current is divided by square root of scan rate) cyclic voltammograms of (a) [NBu_4][**2a**], (b) [NBu_4][**2b**] and (c) overlaid voltammograms of [NBu_4][**2a**] and [NBu_4][**2b**] at 500 mV/s scan rate in 0.3 M NBu_4PF_6 THF solution at room temperature.

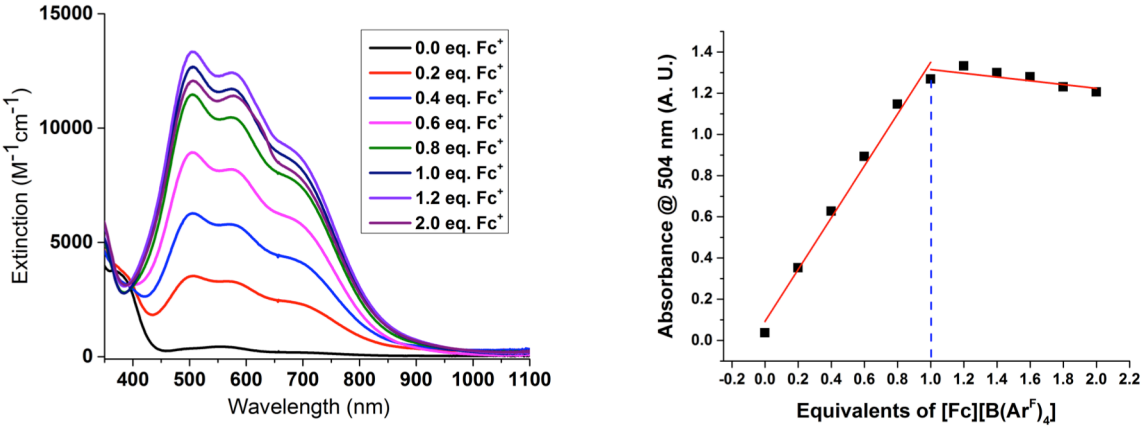

Figure S10. UV-vis absorption spectra upon addition of varying equivalents of $[Fc][B(Ar^F)_4]$ to 0.1 mM THF solution of $[NBu_4]$[**2a**] at -80 °C (left) and plot of corresponding absorbance values at λ = 504 nm as a function of varying equivalents of $[Fc][B(Ar^F)_4]$(right).

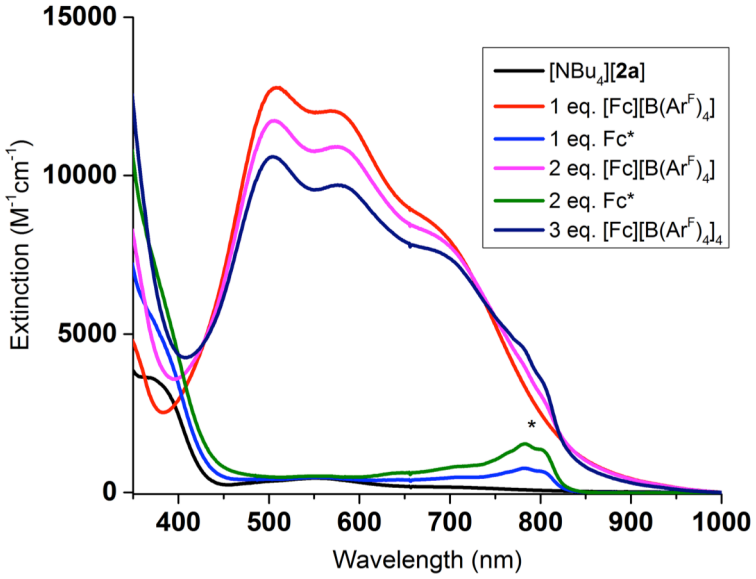

Figure S11. UV-Vis titration of $[Fc][B(Ar^F)_4]$ and decamethyl ferrocene (Fc*) to a 0.1 mM THF solution of $[NBu_4]$[**2a**] at -80 °C (* denotes decamethyl ferrocenium signal).

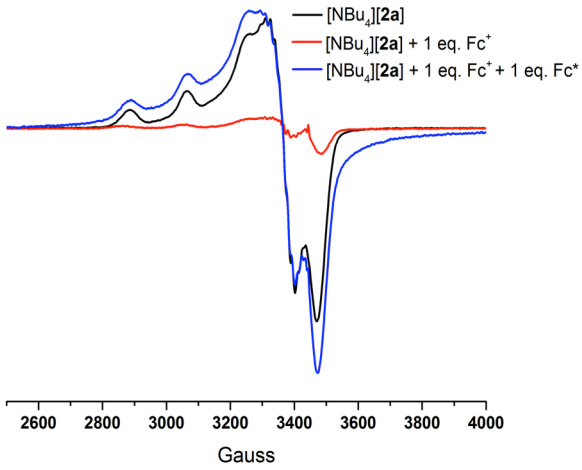

Figure S12. Overlaid EPR spectra of [NBu_4][**2a**], [NBu_4][**2a**] after addition of [Fc][$B(Ar^F)_4$]), and [NBu_4][**2a**] after subsequent addition of [Fc][$B(Ar^F)_4$] and then Fc*. All Spectra taken at 1 mM in THF at 30 K.

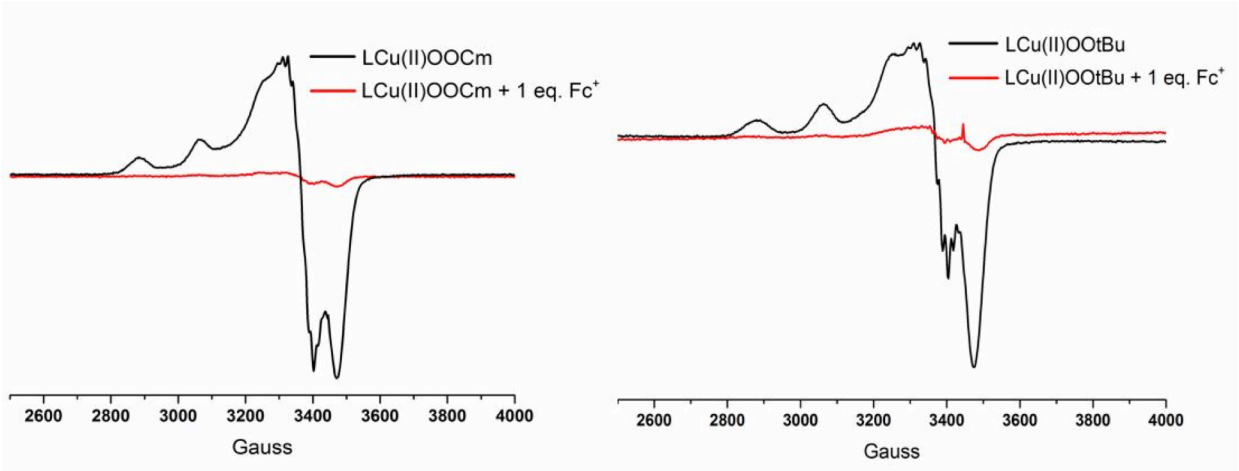

Figure S13. Starting and oxidized EPR spectra of 1 mM [NBu_4][**2a**] (left) and 1 mM [NBu_4][**2b**] (right) at 30 K in THF (oxidation performed using [Fc][$B(Ar^F)_4$]).

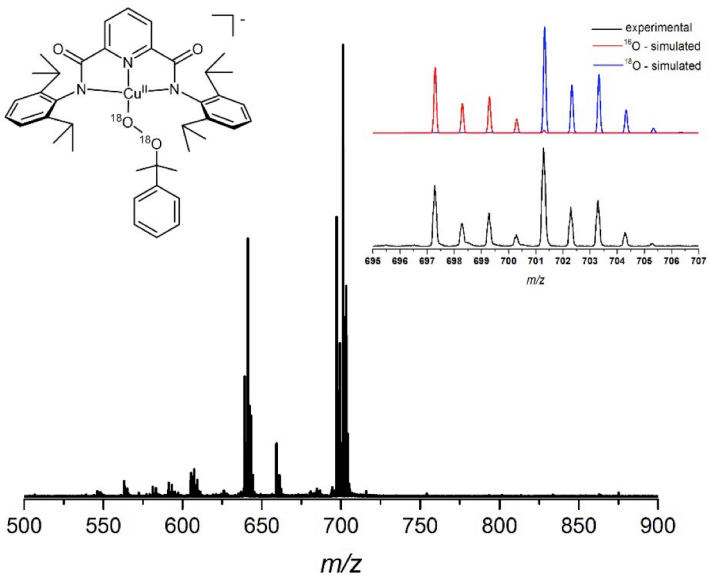

Figure S14. Negative mode low-res ESI-MS of ^{18}O isotopically labeled [NBu_4][**2a**], with simulated isotopic pattern for the parent ion shown in the inset (60% incorporation of label).

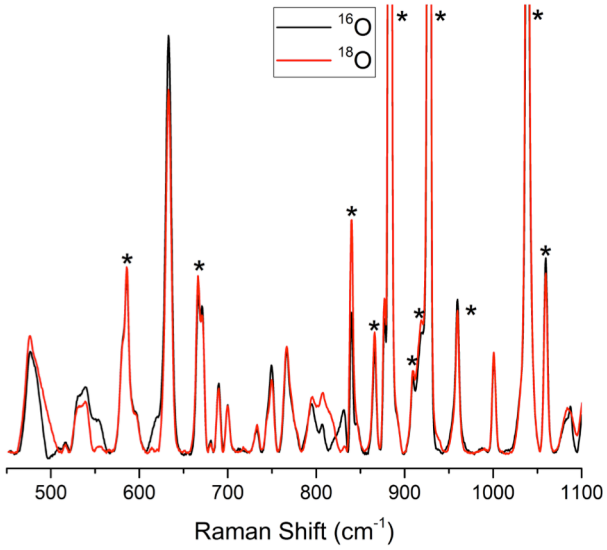

Figure S15. Full resonance Raman spectra of [NBu4][**2a**] with ^{16}O (black) and ^{18}O (red) showing a shift of the peak at 831 cm^{-1} to 813 cm^{-1} (* denotes solvent).

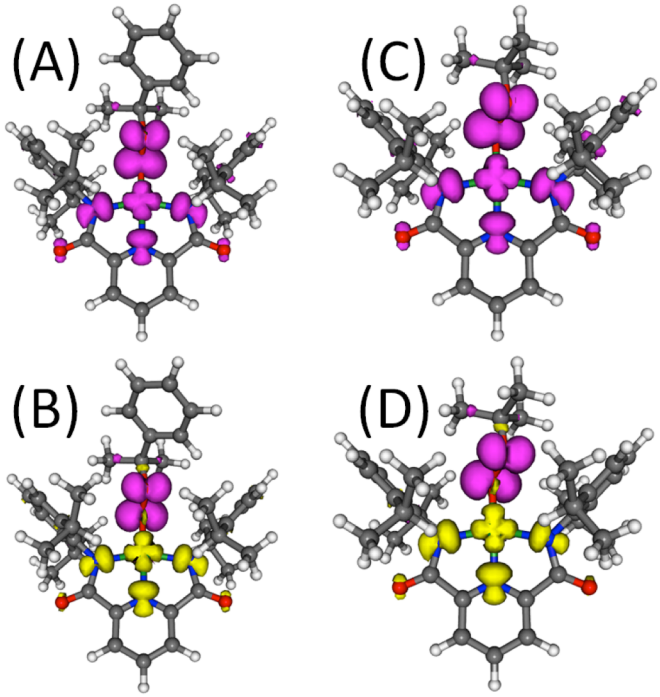

Figure S16. Spin density plots (pink is positive density, yellow is negative density) of $[CuOOR]^{2+}$ for [(A,B) R = cumyl [**2a**]$^{-}$; (C,D) R = tBu [**2b**]$^{-}$] where (A & C) are the triplet states and (B & D) are the broken-symmetry solution singlet states using PBE0 / Def2-TZVP | Def2-QZVP(Cu) level of theory where gray, white, blue, red, and green atoms represent C, H, N, O, and Cu, respectively.

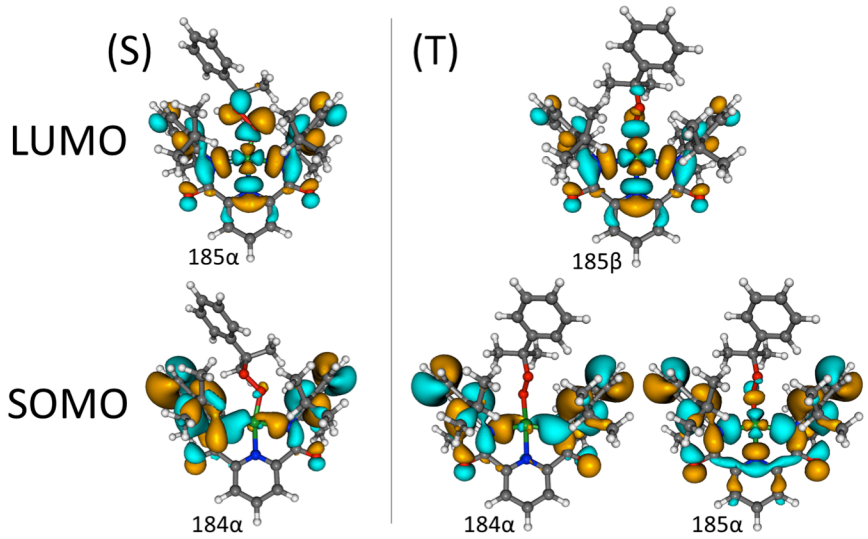

Figure S17. Kohn-Sham molecular orbital plots (orange is positive density, cyan is negative density) of $[CuOOCm]^{2+}$, **3a** where (S) is the singlet state and (T) is the triplet state using PBE0 / Def2-TZVP | Def2-QZVP(Cu) level of theory where gray, white, blue, red, and green atoms represent C, H, N, O, and Cu, respectively. Numbers indicate the orbital level with α = spin up and β = spin down. SOMO is singly occupied molecular orbital and LUMO is lowest unoccupied molecular orbital.

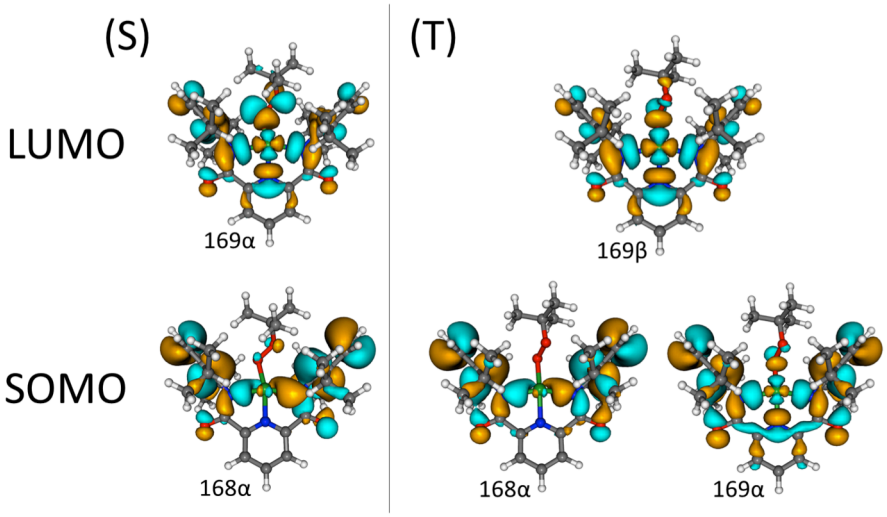

Figure S18. Kohn-Sham molecular orbital plots (orange is positive density, cyan is negative density) of $[CuOOtBu]^{2+}$, **3b** where (S) is the singlet state and (T) is the triplet state using PBE0 / Def2-TZVP | Def2-QZVP(Cu) level of theory where gray, white, blue, red, and green atoms represent C, H, N, O, and Cu, respectively. Numbers indicate the orbital level with α = spin up and β = spin down. SOMO is singly occupied molecular orbital and LUMO is lowest unoccupied molecular orbital.

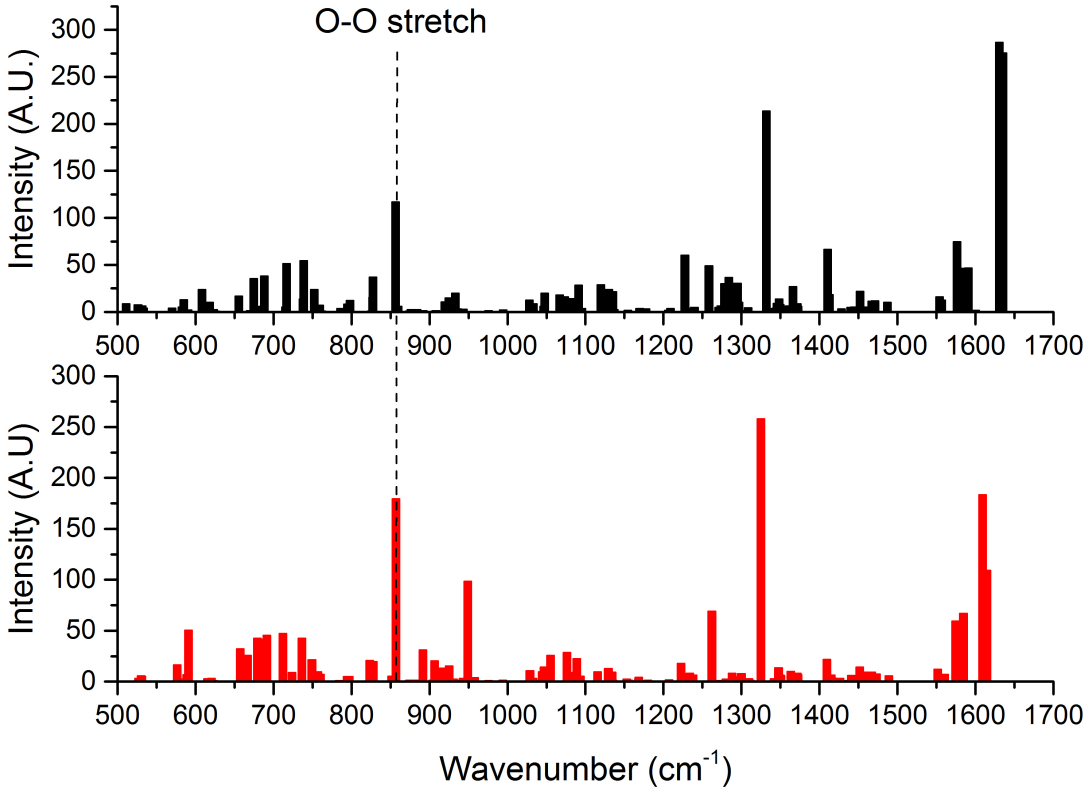

Figure S19. TD-DFT predicted [PBE0 / Def2-TZVP] spectrum of the singlet state (black line) and triplet state (red line) of **3a**.

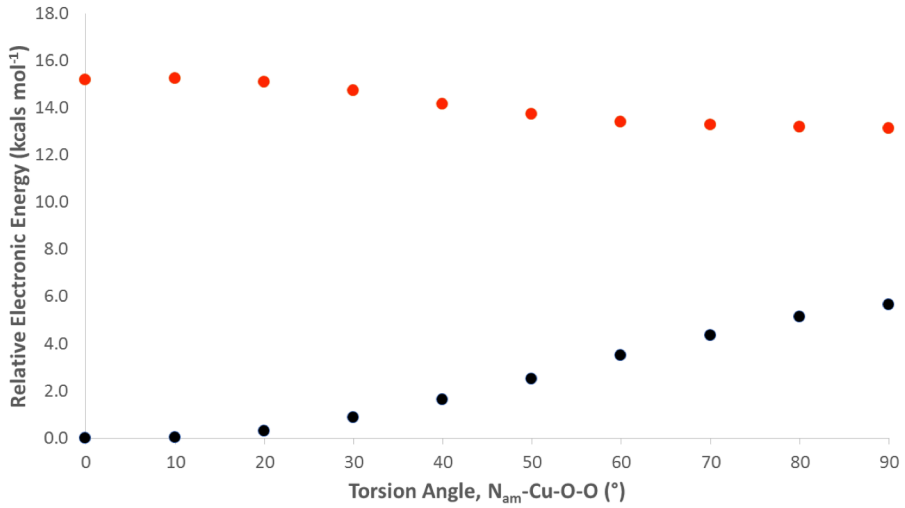

Figure S20. Relaxed surface scan of **3a** [*m*PWPW / Def2-TZVP] tracking the electronic energy of the singlet (black) and triplet (red) states by varying the torsion angle about the N_{amide}-Cu-O-O. Note that the electronic energy of the singlet state has not been spin purified.

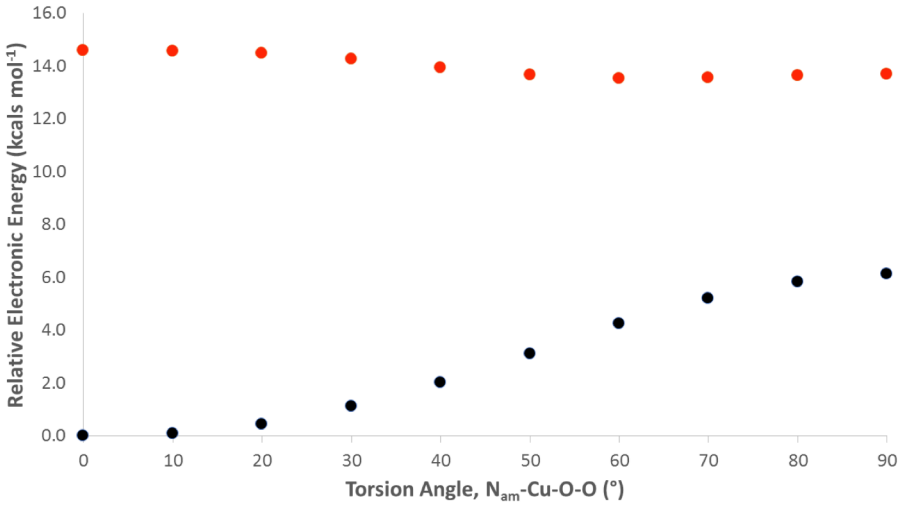

Figure S21. Relaxed surface scan of **3b** [*m*PWPW / Def2-TZVP] tracking the electronic energy of the singlet (black) and triplet (red) states by varying the torsion angle about the N_{amide}-Cu-O-O. Note that the electronic energy of the singlet state has not been spin purified.

Table S3. Functional screen of the broken-symmetry calculations for **3a** (top series) and **3b** (bottom series) starting from the *triplet* state optimized geometry [*m*PWPW / Def2-TZVP | Def2-QZVP(Cu)] where a negative number indicates the singlet state is favored and a positive number means the triplet state is favored for the ground state. Electronic energy of the singlet state (E_S) was spin purified according to eq. 4.

Complex	Functional[a]	E_T (Eh)	E_{BS} (Eh)	$\langle S^2_T \rangle$	$\langle S^2_{BS} \rangle$	Spin Purified E_S (kcals/mol)
3a	*m*PWPW	-3659.545698	-3659.550960	2.005	0.553	-4.6
	BP86	-3659.226612	-3659.230524	2.007	0.562	-3.4
	OLYP	-3659.877159	-3659.882306	2.005	0.553	-4.5
	TPSS	-3659.988592	-3659.993048	2.006	0.575	-3.9
	M06-L	-3659.314125	-3659.316289	2.010	0.580	-1.9
	B3LYP	-3658.284841	-3658.282856	2.010	0.924	2.3
	PBE0	-3656.974595	-3656.972625	2.011	1.008	2.5
	TPSSh	-3659.733747	-3659.733713	2.009	0.765	0.0
	PW6B95	-3663.008901	-3663.006935	2.010	1.008	2.5
	M06	-3658.099305	-3658.095872	2.012	0.937	4.1
	M06-2X	-3658.701729	-3658.700219	2.012	1.010	1.9
	PWPB95	-3664.091592	-3664.090095	2.015	1.014	1.9
Complex	**Functional[a]**	**E_T (Eh)**	**E_{BS} (Eh)**	**$\langle S^2_T \rangle$**	**$\langle S^2_{BS} \rangle$**	**Spin Purified E_S (kcals/mol)**
3b	mPWPW	-3467.773868	-3467.779513	2.005	0.555	-4.9
	BP86	-3467.504909	-3467.509186	2.006	0.564	-3.8
	OLYP	-3468.082143	-3468.087702	2.005	0.555	-4.8
	TPSS	-3468.156636	-3468.161426	2.006	0.577	-4.2
	M06-L	-3467.541244	-3467.543870	2.010	0.590	-2.3
	B3LYP	-3466.607097	-3466.605961	2.010	0.899	1.3
	PBE0	-3465.405376	-3465.403522	2.011	0.994	2.3
	TPSSh	-3467.923568	-3467.924091	2.009	0.774	-0.5
	PW6B95	-3470.953343	-3470.951542	2.010	0.992	2.3
	M06	-3466.450587	-3466.448062	2.012	0.884	2.9
	M06-2X	-3466.975813	-3466.974268	2.012	1.010	2.0
	PWPB95	-3472.438347	-3472.436818	2.016	1.014	2.0

[a] All calculations used the Def2-TZVP | Def2-QZVP(Cu) basis set, see experimental section for further details.

Table S4. Functional screen of the broken-symmetry calculations for **3a** and **3b** starting from the *singlet* state optimized geometry [*m*PWPW / Def2-TZVP | Def2-QZVP(Cu)] where a negative number indicates the singlet state is favored and a positive number means the triplet state is favored for the ground state. Electronic energy of the singlet state (E_S) was spin purified according to eq. 4.

Complex	Functional[a]	E_T (Eh)	E_{BS} (Eh)	$\langle S^2_T \rangle$	$\langle S^2_{BS} \rangle$	Spin Purified E_S (kcals/mol)
3a	*m*PWPW	-3659.529426	-3659.566989	2.005	0.000	-23.7
	M06-L	-3659.303285	-3659.338407	2.011	0.000	-22.1
	PBE0	-3656.952555	-3656.976949	2.012	0.326	-18.4
	M06-2X	-3658.679340	-3658.692578	2.013	0.791	-13.8
3b	*m*PWPW	-3467.757952	-3467.795736	2.005	0.000	-23.8
	M06-L	-3467.529614	-3467.564999	2.011	0.000	-22.3
	PBE0	-3465.38489	-3465.408997	2.012	0.332	-18.2
	M06-2X	-3466.955196	-3466.968200	2.012	0.792	-13.6

[a] All calculations used the Def2-TZVP | Def2-QZVP(Cu) basis set, see experimental section for further details.

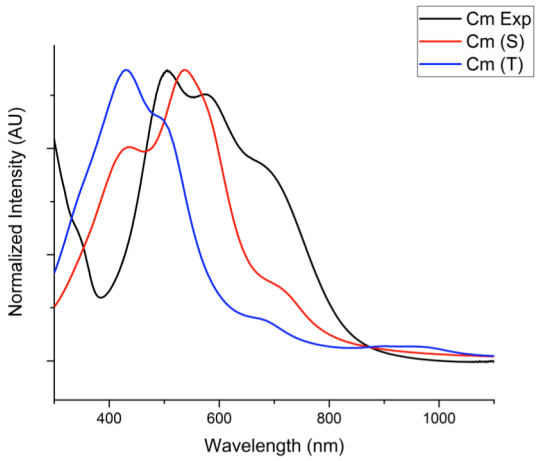

Figure S22. Overlay of **3a** experimental UV-Vis spectrum [THF, -80°C, black line] with the TD-DFT predicted [PBE0 / Def2-TZVP] spectrum of the singlet state (red line) and triplet state (blue line) using a Lorentzian lineshape (half-width = 50 nm), normalized to the λ_{max} of the experimental spectrum.

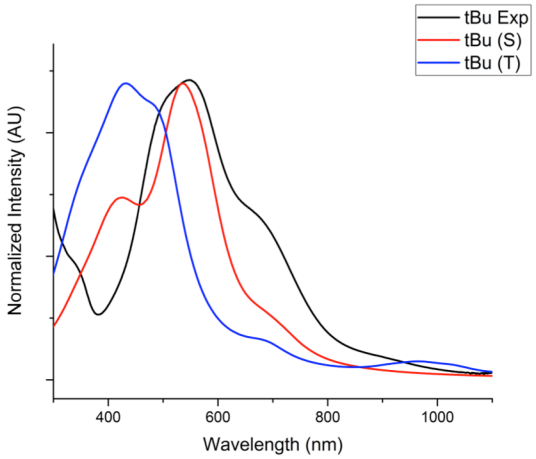

Figure S23. Overlay of **3b** experimental UV-Vis spectrum [THF, -80°C, black line] with the TD-DFT predicted [PBE0 / Def2-TZVP] spectrum of the singlet state (red line) and triplet state (blue line) using a Lorentzian lineshape (half-width = 50 nm), normalized to the λ_{max} of the experimental spectrum.

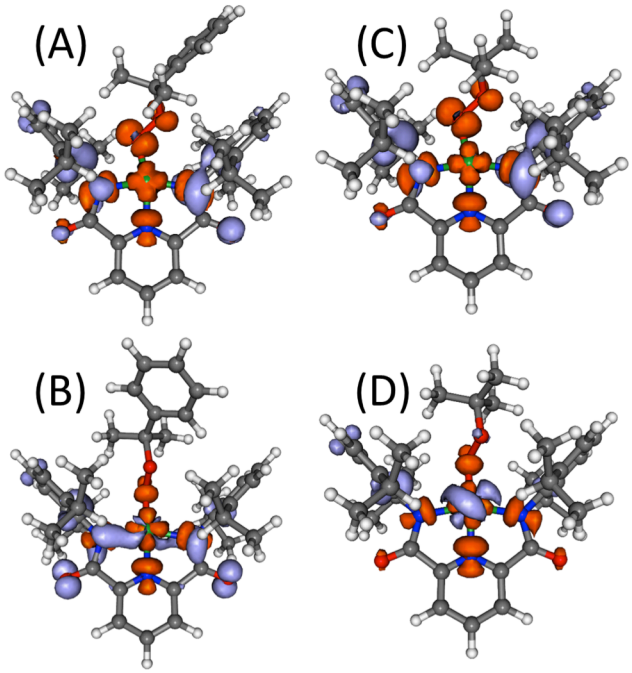

Figure S24. TD-DFT difference density plots of the most intense oscillator strength transition (purple is loss of electron density, orange gain of electron density) of $[CuOOR]^{2+}$ for [(A,B) R = cumyl, **3a**; (C,D) R = tBu, **3b** where (A & C) are the singlet states and (B & D) are the triplet states using PBE0 / Def2-TZVP level of theory where gray, white, blue, red, and green atoms represent C, H, N, O, and Cu, respectively.

Table S5. TD-DFT for **3a,b** in the singlet and triplet states using PBE0 / Def2-TZVP of the first 40 excited states with an oscillator strength threshold of >0.001. Bolded values are pictured as difference density plots in Figure S23.

3a (S)		**3a** (T)		**3b** (S)		**3b** (T)	
Energy (nm)	$f_{osc.}$	Energy (nm)	$f_{osc.}$	Energy (nm)	$f_{osc.}$	Energy (nm)	$f_{osc.}$
722	0.038	1453	0.005	719	0.019	1444	0.009
690	0.020	995	0.001	682	0.027	1177	0.002
605	0.008	972	0.002	579	0.039	1030	0.003
584	0.180	946	0.001	568	0.150	985	0.001
564	0.007	895	0.002	561	0.007	964	0.004
531	**0.262**	685	0.008	**527**	**0.294**	915	0.002
479	0.033	588	0.001	433	0.067	689	0.008
447	0.035	543	0.003	429	0.025	649	0.001
434	0.046	509	0.063	405	0.096	637	0.001
429	0.056	499	0.011	391	0.019	**501**	**0.056**
405	0.067	449	0.018	367	0.002	493	0.027
396	0.031	**430**	**0.072**	364	0.002	466	0.001
370	0.001	425	0.001	360	0.010	453	0.023
364	0.004	408	0.009	347	0.015	427	0.029
360	0.003	395	0.002	344	0.015	425	0.034
351	0.008	394	0.001	342	0.007	405	0.011
347	0.027	393	0.003	338	0.004	396	0.006
		388	0.002			391	0.002
		386	0.017			388	0.003
		377	0.001			382	0.003
		373	0.001			371	0.010
		365	0.002			368	0.002
		359	0.001			365	0.006
		355	0.001			364	0.002
		350	0.001			358	0.001
		348	0.004			351	0.003
		344	0.002			351	0.001
		341	0.017			345	0.002
		338	0.001			345	0.002
		337	0.005			340	0.008
		334	0.001			338	0.004
						335	0.008
						332	0.002
						330	0.006
						328	0.001

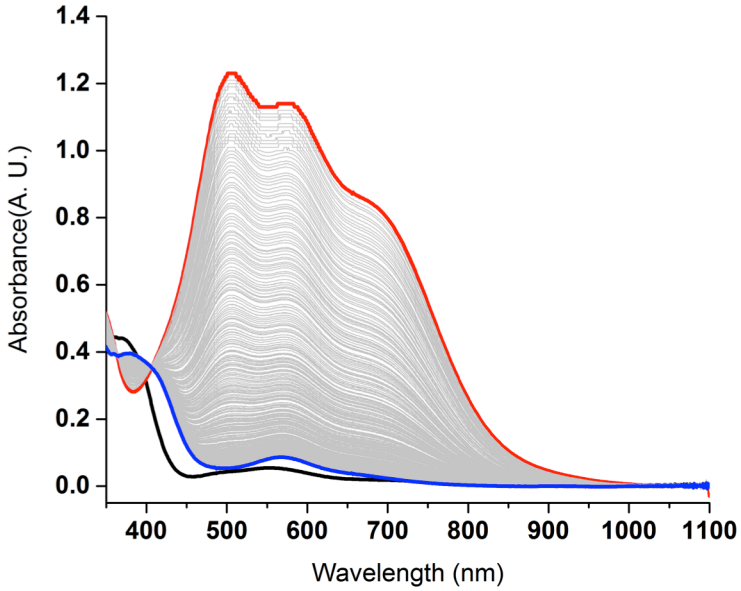

Figure S25. Reaction of 0.1 mM **3a** with 100 equiv. TEMPO-H at -80 °C in THF. Starting spectrum [NBu_4][**2a**] (black), oxidized spectrum **3a** (red), and final decay spectrum (blue).

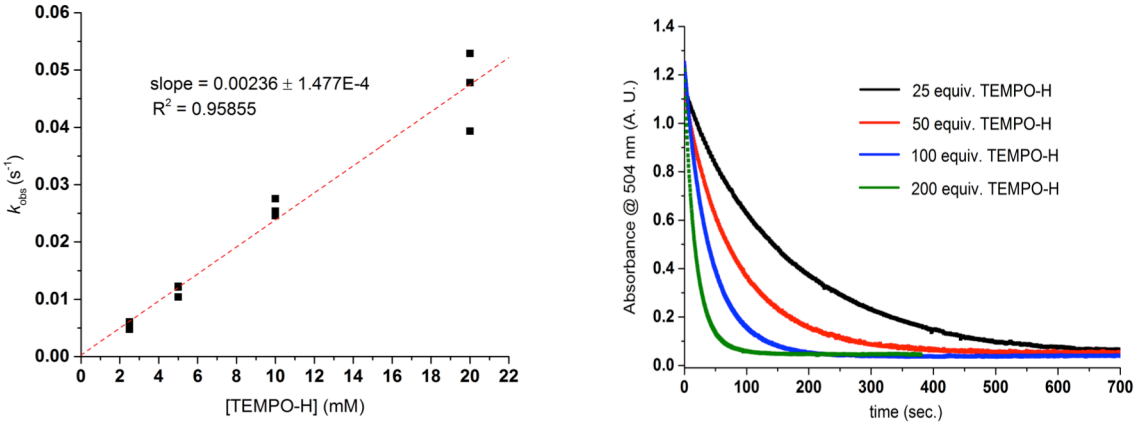

Figure S26. Plot of observed rates of reaction of **3a** with TEMPO-H vs. concentration of TEMPO-H (left). Plot of decay of 504 nm feature over time with varying equivalents of TEMPO-H (right).

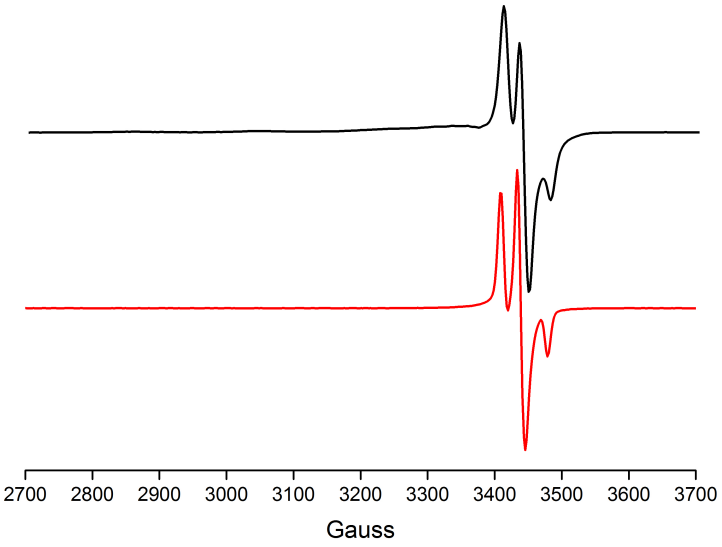

Figure S27. Continuous wave X-band EPR spectra of solution of products of reaction of 1 mM **3a** with TEMPO-H (10 equiv.) at -80 °C (black trace) and 0.5 mM standard of TEMPO• radical (red trace). EPR spectra collected in THF at 30K and 55 dB.

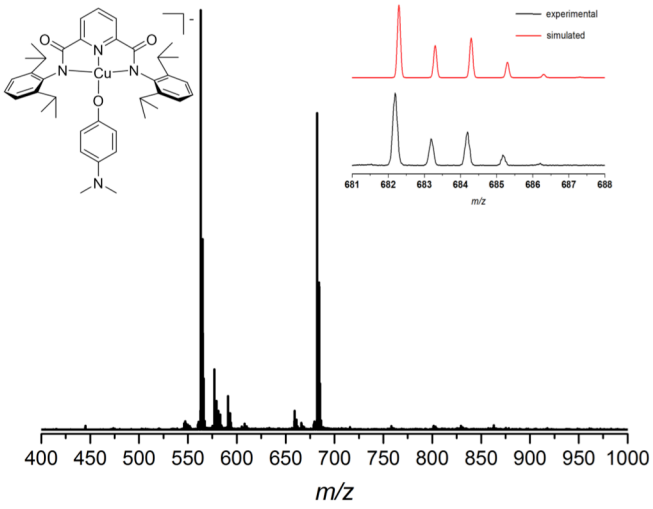

Figure S28: Negative mode Hi-res ESI-MS of [NBu_4][**5**], simulated isotopic patterns inset.

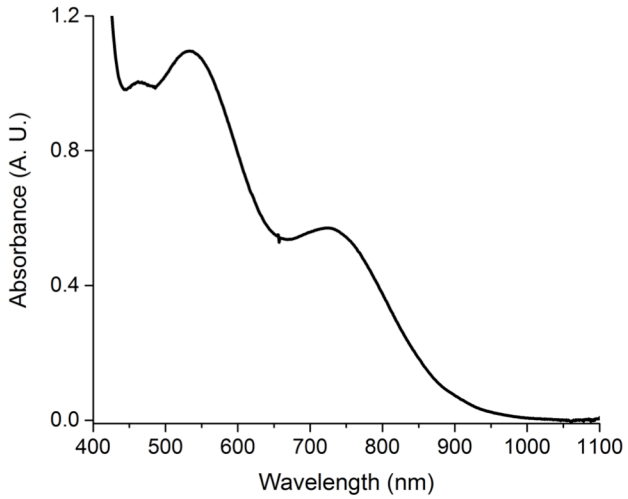

Figure S29. UV-visible spectrum of 1 mM solution of [NBu_4][**5**] in THF at -80 °C.

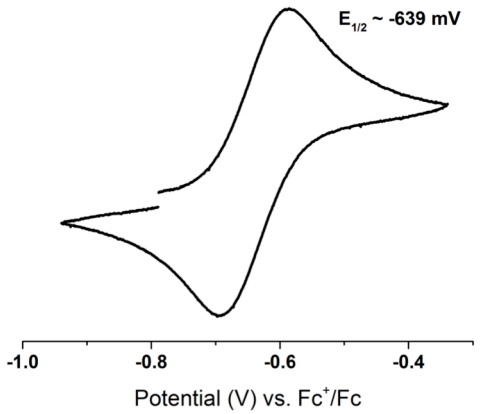

Figure S30. Cyclic voltammogram of 2 mM solution [NBu_4][**5**] in THF (0.3 M NBu_4PF_6) with a scan rate of 50 mV/s.

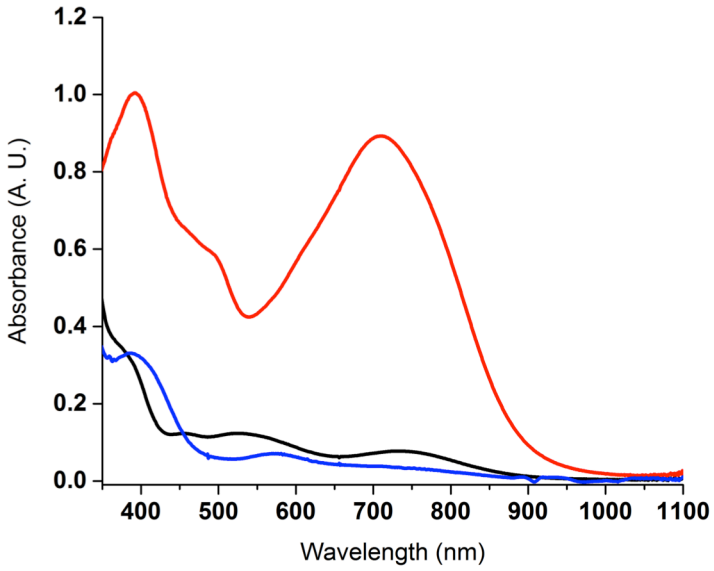

Figure S31. Overlaid UV-vis spectrum of 0.1 mM [NBu_4][**5**] (black), **4** (red), and decay product of **4** (blue) taken at -80 °C in THF.

DFT Geometry Optimized Structures

Table S6. Cartesian coordinates (Å) for **[LCu^{II}-OOCm]$^-$**

Atom	X	Y	Z
Cu	-0.19662246446940	0.29777605978648	-0.21231773163458
O	-1.77373338530120	0.87468114388783	0.63511785770254
O	-1.76719086112923	1.82638904248594	1.72720656166120
N	1.13826908712189	-0.21956277404388	-1.55686910818966
C	2.42054334607672	0.07487712353120	-1.32623664645790
C	3.39975960277324	-0.24926416191328	-2.26596472069561
H	4.43526283974261	0.00529704884249	-2.04896919141164
C	3.00207436143902	-0.89321506449187	-3.44102175194483
H	3.74478792798630	-1.15731456906948	-4.19498667260109
C	1.65626174845164	-1.20961540244198	-3.64682268430671
H	1.29590143581673	-1.72208804397238	-4.53670269288659
C	0.73373680779241	-0.85537942620518	-2.66163728697697
C	-0.74510467381098	-1.15945581871703	-2.72366510759149
N	-1.38109674268976	-0.77587229766552	-1.59686877028048
C	-2.77375128061848	-0.98374027308572	-1.48964664033805
C	-3.68234977765902	-0.02134464137017	-1.99747907655535
C	-5.05526516172734	-0.23898403707217	-1.83988191319598
H	-5.75976051946532	0.49724413118513	-2.23090764593332
C	-5.54106391044026	-1.37319963078419	-1.19446894305634
H	-6.61533491674268	-1.52378008153220	-1.07926258305944
C	-4.64232152078828	-2.31361460675621	-0.69304578140424
H	-5.02556662822833	-3.20144104911624	-0.18850367589124
C	-3.26123640378212	-2.14132668143880	-0.82736743411883
C	-2.29382962451784	-3.20099791696193	-0.32127579114168
H	-1.32370429543345	-2.69971870515241	-0.19229869833238
C	-2.69137849839432	-3.80224256037588	1.03431899355199
H	-2.85049504441925	-3.02157902069629	1.78929002981571
H	-1.89867672009283	-4.47172777187011	1.39801738834231
H	-3.61269203446535	-4.39884243024901	0.96608867586543
C	-2.10204156712343	-4.30866089425641	-1.37618843039987
H	-1.80243702735938	-3.88361979798828	-2.34192671506712
H	-3.04082767304950	-4.86291031536350	-1.52656416230891
H	-1.33277482647306	-5.02628303354290	-1.05271868366288
C	-3.19181817386295	1.22174285238891	-2.72337188623364
H	-2.09865760057227	1.23632148164661	-2.62446404170521
C	-3.72174859024464	2.51542272765892	-2.08519054439865
H	-3.43759732396614	2.56249467321778	-1.02684379843453
H	-4.81732756974665	2.58491015691045	-2.15508361721528
H	-3.30185168761415	3.39428477640758	-2.59656508275402
C	-3.52182720713003	1.15278676149057	-4.22549328539209
H	-3.10297485532777	0.24204668737997	-4.67134920459592
H	-3.10498703090674	2.02356159357069	-4.75363570344548
H	-4.60947000895879	1.14861052252532	-4.39256884816748
O	-1.21286583349606	-1.71790881905948	-3.73753875831498
C	2.69534648041026	0.72487698487146	0.00715798327863
O	3.87175532781420	1.01652419159340	0.30744753832550
N	1.57090370267793	0.89533131229588	0.74061342862245
C	1.71671141662087	1.43238996390689	2.04467421129448
C	1.47073543718060	2.81235390091814	2.26781440421155
C	1.57036532594997	3.31369194988590	3.56904156632221
H	1.37060518966355	4.36917258091330	3.75273316108548
C	1.91630746656583	2.49002799110441	4.63861119489729
H	1.98496521609119	2.90008201513883	5.64709088437595
C	2.17389082356518	1.14116226889961	4.40962397684318
H	2.45788499142874	0.50085428303465	5.24653198136732
C	2.08157280492566	0.58940570723314	3.12618338284440
C	2.42341621117884	-0.87924972355762	2.91059544470505
H	2.09852696855276	-1.13707405818239	1.89326113175522
C	3.94691170377408	-1.09995558311346	2.98242839212150
H	4.46400017863540	-0.44505783128790	2.27136841814032
H	4.19860229148458	-2.14518767318376	2.74683686957712
H	4.32352252494728	-0.88252271289336	3.99337408294618
C	1.69281756471125	-1.82198570643451	3.88033430433915
H	1.92292325567369	-2.86936416935017	3.63631326178986
H	0.60491819436835	-1.69177948556507	3.82702421131768
H	2.00184400872641	-1.65423040274812	4.92221103884531
C	1.16807671172680	3.73422680045439	1.09605793565606
H	0.67629719795529	3.11561866161920	0.33166527200233
C	2.47745861728428	4.27610683439739	0.48661332683495
H	3.17223371178271	3.46485036840674	0.23895587690001
H	2.98265560943946	4.94353143160042	1.20123691416777
H	2.26831924772056	4.85429300477497	-0.42619331060022
C	0.21729315212951	4.88760251224760	1.43766016702967
H	-0.70426013603015	4.51807542778204	1.90148682733302
H	-0.05277197184105	5.43164519765716	0.52110998036336
H	0.68115664401243	5.61569962340867	2.11959073522742
C	-2.55168864245567	1.29015884834701	2.83752059424368
C	-1.80640815593672	0.10863955490089	3.45746435031972
C	-3.94267034685078	0.84931583491977	2.34786154440898
H	-1.63790762275032	-0.63204959106357	2.66746847000816
H	-2.39191963091971	-0.36830586181022	4.25537855597285
H	-0.83478522594993	0.42137120615298	3.85662710266346
H	-3.84200615551884	0.03593183383164	1.62204430608307
H	-4.46699175261609	1.68123561315275	1.86302787232602
H	-4.54697830891270	0.50781926090395	3.19928706546642
C	-2.69924670993772	2.49208985724545	3.77177873720882

C	-2.42059012715125	2.42202481749002	5.14195813122455
C	-3.17005118884926	3.71069905040823	3.25567254081969
C	-3.35781605866884	4.81799631882907	4.08148083579528
C	-3.08537532026038	4.73067639142316	5.44914817846267
C	-2.61640054126887	3.52721795488752	5.97471909025103
H	-2.03905752875162	1.49714142354933	5.57036444216605
H	-3.37442587283041	3.78676867985483	2.18888089954226
H	-3.71616522793217	5.75533751773184	3.65422584509637
H	-3.23254890213748	5.59539950765234	6.09704418860971
H	-2.39010626662119	3.44605915804176	7.03859945857230

Table S7. Cartesian coordinates (Å) for **[LCu^{II}-OOtBu]$^{-}$**

Atom	X	Y	Z
C	3.09910699654014	13.96878942866490	10.37195195964152
H	2.68039262821946	14.95983190414300	10.14552858084694
H	2.92639899917339	13.30706583563989	9.51637288160067
H	4.18268102778830	14.07307565771763	10.51714367652990
C	2.77022789304713	14.24107103555075	12.86304403563728
H	3.85612372258216	14.34084509515394	12.99099561440922
H	2.35223068947332	13.78680962382728	13.76973573422451
H	2.34209264578757	15.24541640637735	12.74134651407479
C	0.93659846565174	13.22986971476084	11.45492894256141
H	0.73385997947762	12.51192944656193	10.65252031820813
H	0.47351847360454	14.19176172137453	11.19342767956038
H	0.48310371416421	12.86259406887759	12.38358366261326
Cu	2.34793964678739	9.42987792647916	11.18637989939431
N	2.41819099308560	8.99633574447313	9.12266638562776
O	2.60413554343623	7.14474922949818	7.69586738779529
C	2.29261122627647	6.81420588715119	10.03808287845873
N	2.20048844614265	7.47552428082305	11.19724017413023
C	2.46254833162113	7.68324822456232	8.81342808072632
C	2.21592546953274	5.42122088079407	10.01511692926159
H	2.29946606347139	4.91155542047370	9.05716193487102
C	2.57392801121516	9.95142881108306	8.09355623444920
C	3.86852721036250	10.37919343463413	7.70549821823646
C	3.98720906260334	11.36105349242770	6.71581638724590
H	4.98153072466626	11.69334298365072	6.41222722017617
C	1.42477592285085	10.51987265516641	7.48311427494819
C	2.86516916625803	11.92306702948798	6.11246289491289
H	2.97849013508656	12.68976022820259	5.34470586298349
C	5.11948439404665	9.77512667764745	8.32501387461800
H	4.78595263770670	9.12506522150162	9.14421853422380
C	2.03280965746763	4.74589250203635	11.22515293798468
H	1.97053118345695	3.65692779325011	11.23685048281369
C	1.59476171166406	11.49931821990875	6.49988785018367
H	0.71755880356926	11.94012886715318	6.02466115953243
C	0.03444749446250	10.02863356455601	7.85829932008783
H	0.12057192244897	9.59084212405972	8.86337530493570
C	-0.41907385192936	8.90490580601055	6.90517875600810
H	-0.54833965627663	9.29590559799388	5.88458068118628
H	-1.38189115791123	8.48252054392487	7.23086663239451
H	0.32373543105252	8.09883837161592	6.86659388412668
C	2.44874471715168	13.38732282855886	11.63302667972903
C	-1.01871047204068	11.14366774429796	7.92414168302770
H	-1.22926632651780	11.57048899359481	6.93268995279821
H	-0.69853093036620	11.96143309738426	8.58241634890427
H	-1.96694709624305	10.74502702070225	8.31246858919675
C	6.03945133591931	10.84145061375727	8.93988801018147
H	6.42555132308073	11.53488278067880	8.17821390218623
H	6.90586907299272	10.36595392858692	9.42314282931994
H	5.49752479234413	11.42239620431586	9.69598925485232
C	5.86936414946132	8.89467238841927	7.30874180127380
H	6.24189942663327	9.49390267649017	6.46431733264123
H	5.20773484182778	8.11534520203615	6.91046716295300
H	6.73540525192419	8.40870909471265	7.78284415989894
O	2.87982551630080	11.19496962424583	10.85068289436124
O	3.05631231158985	12.10964430807664	11.96118420694779
N	1.92546695466651	9.07654835965578	13.21353187025425
O	1.69524172430598	7.26814470717245	14.68869286843388
C	2.00636181399783	6.85534126360930	12.36483588418379
C	1.86494855954895	7.76937821460075	13.55743033303742
C	1.92029858972837	5.46378957334018	12.41920807947774
H	1.76576923299044	4.98860101691883	13.38591995458848
C	1.75533686348959	10.03052192248325	14.24774032810053
C	0.45231912452359	10.47710523285321	14.59093591046179
C	0.31191775526579	11.44605959571077	15.59100538526104
H	-0.68596273425497	11.79280811519255	15.86363479388358
C	2.88739591684656	10.55194314280893	14.92457465181425
C	1.42004045973947	11.96733590902840	16.25516733598585
H	1.29050938676093	12.72106567930029	17.03322083784946
C	-0.78177462077434	9.86548110723195	13.94062868146789
H	-0.43967013266960	9.36432962003545	13.02420261852412
C	2.69462730178627	11.51430917436695	15.92083593620633
H	3.56009829653766	11.91845957294076	16.44759330142392
C	4.28366261658553	10.02998104379734	14.61957823031873
H	4.22663338494262	9.53614376757558	13.63990052985099
C	4.69686934859543	8.96453294481406	15.65426297867960
H	4.79715138697090	9.41404342547375	16.65392773207135
H	5.66684001781686	8.51931383706618	15.38557883737256
H	3.94785137908942	8.16546296251036	15.71471035501306
C	5.34173019105647	11.13675533391000	14.51161322113010
H	5.49803606686218	11.65312072251418	15.47025658932139
H	5.05135352766533	11.87771503328998	13.75762296456596

H	6.30840049553023	10.70441775201908	14.21480766804978
C	-1.84501828870818	10.89768579292439	13.53651908193924
H	-2.27819718291549	11.40408165047162	14.41118178683834
H	-2.67101714126163	10.40058614260144	13.00756591671268
H	-1.43162714148872	11.66606977934254	12.87157060476526
C	-1.39569791402427	8.78816995586594	14.85725792882440
H	-1.78643619613980	9.24435369017754	15.77950202727299
H	-0.64369881945348	8.04052035205954	15.13635642889297
H	-2.23068789633445	8.27916564326343	14.35215975793306

Table S8. Cartesian coordinates (Å) for **LCu^{III}-OOCm (S)**

Atom	X	Y	Z
Cu	-0.12497714170391	0.19067115967068	-0.25998899094128
O	-1.68125288275168	0.76521329013202	0.58144128818186
O	-1.68585877626397	1.63975739216682	1.68313370668530
N	1.18961684145763	-0.35600315528198	-1.53472453564114
C	2.45955703286708	-0.03604631260822	-1.29529459969931
C	3.44981496747254	-0.38688364447476	-2.21052815702640
H	4.48207836836259	-0.11709826161300	-1.99653721964844
C	3.06628981623338	-1.07353092366299	-3.36659827366868
H	3.81834092976199	-1.36080468403753	-4.10085429456815
C	1.72260445782700	-1.39395837158512	-3.58548396301619
H	1.37757027170406	-1.92484741091016	-4.47060331352527
C	0.78926868948464	-1.01134424744682	-2.62492862975698
C	-0.69436994646297	-1.25332383208278	-2.67759945872535
N	-1.30895868643081	-0.78009659393202	-1.55537174621489
C	-2.70468158142711	-0.85944775633485	-1.40250346876189
C	-3.52451530262041	0.20639043569945	-1.86713504125507
C	-4.90818154819741	0.10172850571250	-1.69616709150891
H	-5.55371720978680	0.90378397471855	-2.05371919583450
C	-5.47711034762744	-1.01132892947145	-1.08468589705800
H	-6.55869950368570	-1.07365844421346	-0.96324380790857
C	-4.66476231811169	-2.05053138316001	-0.62860561216921
H	-5.12547986229384	-2.91928971951035	-0.15924929897271
C	-3.27745904979961	-1.99876535148199	-0.76825407791240
C	-2.41487058585119	-3.16686411145726	-0.31707425143614
H	-1.38496798828288	-2.79199949813975	-0.23092338778053
C	-2.82073434965219	-3.73150242695883	1.05262885506069
H	-2.85399397619286	-2.94991339667934	1.82208412389733
H	-2.09790670778521	-4.49409987943787	1.37285424052932
H	-3.80657565845117	-4.21512077735634	1.02082132372608
C	-2.41520338616431	-4.28053290946298	-1.38442347473825
H	-2.11284087661558	-3.89449664367203	-2.36488609600457
H	-3.41979384375847	-4.71518982357833	-1.48610089435336
H	-1.72602763584784	-5.08718496734378	-1.09694536482427
C	-2.94099412468983	1.40586116973725	-2.59492746932075
H	-1.85116614107331	1.36782288855818	-2.46566673768169
C	-3.42309412368683	2.74444894499411	-2.01483529076708
H	-3.19344222868324	2.81363661084466	-0.94477518979669
H	-4.50549326818526	2.88049623878611	-2.14538182913516
H	-2.92570179202891	3.57869530158940	-2.52842543808201
C	-3.23307271692525	1.31396174265990	-4.10567884330242
H	-2.86269336728878	0.37020588891273	-4.52419356079481
H	-2.75050697201503	2.14476130558896	-4.63945004659595
H	-4.31322112464423	1.37183178099164	-4.30087330304154
O	-1.21788494751675	-1.81655890147071	-3.64413088329974
C	2.66779374740304	0.68649227266709	0.00481648055474
O	3.79931572469439	1.04132580364384	0.35162591747381
N	1.49481955442309	0.86854864867491	0.68683094519404
C	1.55217627266521	1.46191602152307	1.96977643262799
C	1.21756025180913	2.83697946766052	2.11396474565458
C	1.27208084167460	3.40297820575087	3.39013291985904
H	1.01141472221546	4.45149427837890	3.52408384097620
C	1.65788307423493	2.65018759091758	4.49637900557285
H	1.69266375858520	3.11176928533147	5.48325911164824
C	2.00919356617727	1.31103202083890	4.34052139880224
H	2.33680166559366	0.74051380970031	5.20999524531171
C	1.96730184864183	0.68853257261779	3.08963565773080
C	2.44778597458399	-0.75122897072401	2.95541386368344
H	2.21984205710481	-1.08280615475550	1.93330989942529
C	3.97680075379663	-0.82591571887161	3.14219548492485
H	4.49138430636311	-0.14786225559021	2.45255307170504
H	4.33368637660475	-1.84944800532471	2.95943917578764
H	4.25622585307644	-0.55247536659369	4.16952995976432
C	1.74634961580672	-1.72248938747482	3.91961184901540
H	2.12098772262708	-2.74318283317937	3.76133698033311
H	0.66015971031250	-1.73496052341081	3.77123140682095
H	1.94085813707197	-1.46345026818462	4.96934610769531
C	0.90416484678736	3.69236810904791	0.89633131931577
H	0.45960534942727	3.02852666233600	0.14087187628251
C	2.20814632839543	4.26705718026533	0.30292431178915
H	2.94619856700236	3.48342827286288	0.09699308868059
H	2.66537776010355	4.97726247397430	1.00647189385789
H	1.99705666786752	4.80629342980655	-0.63148521423200
C	-0.09842847833702	4.82127090829489	1.16499038371932
H	-1.01311996185548	4.44279823532103	1.63439984322616
H	-0.37168982684067	5.30716401515720	0.21843184119447
H	0.32526563229639	5.60022838023008	1.81413038632906
C	-2.46718548683860	1.05615653943614	2.81350179214531
C	-1.70898830518214	-0.13916471901520	3.37305423347079
C	-3.85341765442724	0.63840282141058	2.30743006812685
H	-1.55765047767399	-0.86702936214802	2.56781558355593
H	-2.28466932339434	-0.63153961288619	4.16690004660837

H	-0.73338798418714	0.16037997690226	3.76894773113227
H	-3.76884737725784	-0.16775283045129	1.57167132244639
H	-4.37560666344406	1.48188796812992	1.84294516241428
H	-4.45584585167411	0.28779570524659	3.15505432833977
C	-2.58793563154781	2.23586268993301	3.77460122652196
C	-2.21802190205537	2.14287416651107	5.12150797274086
C	-3.13032433806825	3.44752889017715	3.31655719623043
C	-3.29186873334116	4.53242255379791	4.17660151506597
C	-2.92629575627322	4.42353254616613	5.52003707171578
C	-2.39183897274625	3.22392121276524	5.98871284094923
H	-1.78960097899524	1.22063337393913	5.50842421502820
H	-3.42149049293013	3.54314443414211	2.27158219118898
H	-3.70832898453573	5.46528914178536	3.79677275901784
H	-3.05871481638797	5.26802465151396	6.19598674171839
H	-2.10251409202028	3.12583741835383	7.03499196754556

Table S9. Cartesian coordinates (Å) for **LCu^{III}-OOtBu (S)**

Atom	X	Y	Z
C	2.63575524817496	13.81723221489649	10.19596110119803
H	2.12762931854015	14.77062556381121	9.99968451211465
H	2.41129675403895	13.12708062637898	9.37604336312273
H	3.71742593769813	14.00000358417354	10.21348533212745
C	2.55792473285901	14.15725540236785	12.69853919838904
H	3.63991045792576	14.33872897645995	12.70460261328932
H	2.26761672495773	13.71563518454397	13.65856137606099
H	2.04959496187655	15.12383258887880	12.58981741944597
C	0.67179559281795	12.94609516991449	11.53623537796888
H	0.43607226699454	12.18689338875457	10.78189532203073
H	0.10367356437858	13.85451769525229	11.29746319148308
H	0.35537867535799	12.58659019409307	12.52142228919395
Cu	2.25879247480538	9.31877738109201	11.16423601048653
N	2.39405828306257	8.97421079187071	9.19735237629970
O	2.51059386723292	7.19568499750670	7.69138729297586
C	2.14196152982088	6.76654900258527	10.01454790837477
N	2.06070790357783	7.42117057421014	11.17351050303972
C	2.37025383049941	7.66125251516476	8.82655869587774
C	2.03077301411951	5.37828073735814	9.99412021540274
H	2.10263665042854	4.85940015740381	9.04021708670630
C	2.64840185492585	9.99394613094857	8.26274215486092
C	3.98797208104090	10.41278726364094	8.02861833797805
C	4.21055335309451	11.43511874078559	7.10122233067594
H	5.23026469970959	11.76393170994475	6.90190680665296
C	1.56051153712593	10.60840125046837	7.57891101556629
C	3.15439777143844	12.03635099738626	6.42350114076421
H	3.35036522422805	12.83124784046893	5.70361809779134
C	5.16851849202043	9.73540716198229	8.70448282131698
H	4.76716584845621	9.10653120388262	9.51033495309465
C	1.83514029000165	4.71272647275998	11.20863314461188
H	1.74454828818160	3.62698951476334	11.22275651034586
C	1.84337128405389	11.62174616104734	6.66241016205273
H	1.02770778998962	12.09647315427822	6.11790168863040
C	0.13138797045656	10.12875362801821	7.77842936000359
H	0.10284621890202	9.59094538889869	8.73693136603917
C	-0.25840662940929	9.12610297500681	6.67255621475596
H	-0.27725568910383	9.62370303585178	5.69251077534016
H	-1.26069181803618	8.71663933847511	6.86256460128428
H	0.45452860230825	8.29532693733978	6.61689071551311
C	2.16540568299649	13.24814559311361	11.53504053592162
C	-0.89246035533628	11.27127061571010	7.85418219458935
H	-0.99580520018379	11.79310905679413	6.89303629413524
H	-0.61919794215630	12.01491120395357	8.61327503166470
H	-1.88243497292440	10.87049605002416	8.11081667021266
C	6.14009660283010	10.73671032310742	9.34780816548979
H	6.62639157762225	11.37478194678137	8.59711330331417
H	6.93565501327014	10.19916125955342	9.88195012600979
H	5.62055091554966	11.38344036859734	10.06488918855776
C	5.89786393912425	8.80877538678057	7.71152140709772
H	6.34253666721888	9.38773032645462	6.88980106071112
H	5.21008639692413	8.07418255329886	7.27519581322625
H	6.70915886983336	8.26804289136971	8.21890079051828
O	2.76375711650820	11.06809051425336	10.80592005409117
O	2.93525594408053	12.01648403410616	11.82835234021182
N	1.93490124193217	9.07314603520251	13.11778656328019
O	1.65354240386232	7.34162466223783	14.65980285135312
C	1.87655611615155	6.81939684871169	12.34690813483336
C	1.80965913254422	7.76767729772069	13.51061011703289
C	1.75669729198472	5.43247153523874	12.40496707856543
H	1.60710176071860	4.95809357009755	13.37281815268517
C	1.80842970278819	10.08058668354665	14.10421422599662
C	0.51610339751275	10.47286648342171	14.55232859481789
C	0.43093790821498	11.46440555088519	15.53438830015385
H	-0.54926759592637	11.77101432250585	15.89988418396411
C	2.98114051794538	10.66423952902735	14.65715316544429
C	1.57369088662973	12.05060320666106	16.07437762330975
H	1.48137863383633	12.81774423610441	16.84354743802355
C	-0.75602336031313	9.78362302410193	14.07420891855310
H	-0.48767797187012	9.15330717708872	13.21548342339128
C	2.83434917994932	11.64615067047995	15.64082246056657
H	3.72099355185604	12.10067523214857	16.08091739861699
C	4.36314276725630	10.16861771296843	14.26092023980184
H	4.27514510056041	9.73772801429765	13.25365021392280
C	4.81261463309060	9.03990532033210	15.21225081226633
H	4.95600462495878	9.43077469603556	16.22966559588576

H	5.76875741515737	8.61407900617869	14.87635366810641
H	4.06999491408857	8.23523056525317	15.26660274697656
C	5.42586781359514	11.27355849206181	14.19513457812611
H	5.64790394638326	11.69165524063097	15.18673223974987
H	5.11111231780550	12.09037383110732	13.53560320248461
H	6.36579573473698	10.86154445176386	13.80355330961658
C	-1.84649323143164	10.76030629348767	13.60440193170252
H	-2.18248070089278	11.41780228949407	14.41775635070865
H	-2.72480677535960	10.19969211801115	13.25606870595242
H	-1.50249331863177	11.39403190546427	12.77861589400994
C	-1.30924931365805	8.85936494499760	15.17846430786652
H	-1.64246555713017	9.44732540473390	16.04541115060769
H	-0.54707110281938	8.14861101912316	15.51631305852556
H	-2.17471127943495	8.29430485231522	14.80424700448335

Table S10. Cartesian coordinates (Å) for **LCu^{III}-OOCm (T)**

Atom	X	Y	Z
Cu	0.04932526425993	0.01919846331065	-0.00410422824864
O	-0.96192223273794	-0.05204108108667	1.63744243487470
O	-1.76589378130259	1.02247910291181	1.88109330598892
N	1.21048966729214	-0.23629598120468	-1.56299304693852
C	2.51304293137540	0.00851189046552	-1.42600135387577
C	3.37635803545336	-0.18683933245181	-2.50311326986090
H	4.43717783780297	0.01696496449364	-2.37231010761279
C	2.83255049380364	-0.63302490527943	-3.71167523111578
H	3.48254428590823	-0.79441373952278	-4.57135655727422
C	1.45833752102639	-0.86424137286640	-3.82623854141357
H	0.99049912271030	-1.19760697488284	-4.75032212276569
C	0.65983261608285	-0.64884140743456	-2.70374907883823
C	-0.83825243819827	-0.80786361061044	-2.65018895397616
N	-1.34136399915308	-0.54308736828837	-1.41380974413691
C	-2.74104786922321	-0.55287064484881	-1.21572745236093
C	-3.51888591187596	0.57617866292866	-1.58873951372418
C	-4.89648618932155	0.54539738867280	-1.34482357497448
H	-5.50879471965922	1.39889844165786	-1.63775691881741
C	-5.50180488760856	-0.55671317521938	-0.74717557277217
H	-6.57691263403339	-0.56002903202734	-0.56642334623651
C	-4.73059346156215	-1.66460110589710	-0.39247071061751
H	-5.21766336469500	-2.52939036910558	0.05673190485024
C	-3.35270545506236	-1.69134208710304	-0.62054488716065
C	-2.53566689169357	-2.93948500742108	-0.32237219832126
H	-1.50524151046869	-2.60790720615580	-0.12493246748359
C	-3.01571098397783	-3.72891575531221	0.90249527275062
H	-3.09251841389441	-3.09527751065582	1.79463624715398
H	-2.30955759889637	-4.54077630243142	1.12272149490780
H	-3.99595738497797	-4.19519865549221	0.73217834214874
C	-2.49256612527039	-3.85571740841850	-1.56360368799865
H	-2.14866460657763	-3.31673954670875	-2.45379496290859
H	-3.49553772405878	-4.25105428536389	-1.77897525510468
H	-1.82254111814941	-4.70928393822464	-1.38791839007812
C	-2.90596242888331	1.78204353469672	-2.28516576925073
H	-1.81612551408582	1.64730883158404	-2.27504728571396
C	-3.20971648963241	3.10413023992489	-1.56152861754905
H	-2.87077895152806	3.08164319440787	-0.51837403510568
H	-4.28536432800100	3.32865695127667	-1.56135657042999
H	-2.70242041864008	3.93712385540182	-2.06753324859738
C	-3.35105852718325	1.84365225553504	-3.75895056765756
H	-3.10573533280790	0.91134026376840	-4.28073340438813
H	-2.84975308563045	2.67463717031791	-4.27499535652761
H	-4.43536190213145	2.00731752344215	-3.83599795877629
O	-1.46556684564501	-1.14309324802682	-3.66444252772891
C	2.91106361033806	0.51549889511516	-0.06297282251833
O	4.09721155446596	0.77524533266866	0.18343709492440
N	1.84449858468120	0.64423510991511	0.77086294121383
C	2.05941454491608	1.13610451471569	2.08380402483060
C	1.87211731643676	2.51834114620270	2.34821865946676
C	2.07792635970293	2.98238442890398	3.65202154947306
H	1.95089308789654	4.04303320029634	3.86887915613526
C	2.45625377227150	2.11708753190958	4.67624364508496
H	2.61800812005339	2.49966400456118	5.68420511892444
C	2.63599203003496	0.76260259783041	4.40499902071235
H	2.94566798117344	0.09348950628754	5.20855776398847
C	2.44333298373022	0.24608733885235	3.11949789975614
C	2.69747914741271	-1.23067783578207	2.85393227271675
H	2.38231860813394	-1.43462496426046	1.82171105297349
C	4.20039335751880	-1.55406670632779	2.94959121272325
H	4.78033395462457	-0.91643407135226	2.27195130524857
H	4.38526231628402	-2.60454838210134	2.68379443974749
H	4.57316702509736	-1.39648449961190	3.97166892514996
C	1.87521325890278	-2.14732817105827	3.77457357545979
H	2.05225655626858	-3.20133227050816	3.51932766683714
H	0.79912819295454	-1.95235411583146	3.67731780858326
H	2.14884959793159	-2.01497192882694	4.83039039925695
C	1.52960704406318	3.49472921559350	1.23253325524299
H	1.13331823865905	2.90151342282617	0.39604360927673
C	2.80458471201029	4.20180655469299	0.73034510841996
H	3.56981973653207	3.47629577255945	0.42940303643174
H	3.23239823966689	4.83392419662433	1.52155646809172
H	2.57496476927796	4.84661728548025	-0.12987407543109
C	0.45392032644401	4.51902115080053	1.62287691434624
H	-0.45881054625434	4.02954979377520	1.98579798079187
H	0.18537909815072	5.13246650248076	0.75199647300653
H	0.80527599616354	5.20606788563260	2.40499029129561

C	-2.41909063295543	0.92973932367536	3.25409321566801
C	-1.30366613445856	0.98819046913421	4.28829170987597
C	-3.18778811654650	-0.38806664632644	3.33556541739205
H	-0.63082708479337	0.13653695542609	4.14845741867248
H	-1.72805591888100	0.92485214905905	5.29787341517726
H	-0.71365351341296	1.90687240437708	4.20437767114375
H	-2.49448458588037	-1.23482714430779	3.28723312398955
H	-3.92050298222654	-0.47776205151847	2.52676108592641
H	-3.72217949057142	-0.42584714752021	4.29281231616531
C	-3.35120367617058	2.13262515068774	3.23965259250305
C	-3.27912328378801	3.13487507109500	4.21595118545346
C	-4.33118380234233	2.23950528979202	2.23978754129150
C	-5.21240942717339	3.31917284138346	2.21930468604784
C	-5.13894785515660	4.30642551720162	3.20397160754106
C	-4.17041957367977	4.20961402057818	4.20253710453827
H	-2.52783012366930	3.08242162694881	5.00120223194578
H	-4.39962377835881	1.48137949790111	1.46031271362286
H	-5.96096659268916	3.38732784051240	1.43048182847258
H	-5.83190631804598	5.14726340372062	3.19116714645699
H	-4.10134133389130	4.97532730336018	4.97477172962099

Table S11. Cartesian coordinates (Å) for **LCu^{III}-OOtBu (T)**

Atom	X	Y	Z
C	3.39368382795029	13.71158960485348	12.27241903099135
H	3.64893010475102	14.77874178546255	12.25408189629715
H	4.23496300688349	13.14999897322647	11.85245150058742
H	3.24419022046014	13.40602760655565	13.31465497293083
C	0.92135133500528	14.20592876628754	12.04699465889488
H	0.77238850516166	13.92598340280203	13.09635539351060
H	0.00894690671033	13.97951340808151	11.48214859198091
H	1.09178110134841	15.28857815292105	11.99774732107483
C	2.31862956748468	13.79278903700685	9.97232001919224
H	3.12074401199351	13.18218054505615	9.54465011374439
H	2.58623328603147	14.85075372569334	9.85421689892840
H	1.39856423775043	13.60339268162332	9.40739493275842
Cu	2.30418157338916	9.32649486982165	11.22067639858639
N	2.38875205736863	8.95178120310559	9.21319460100747
O	2.49899947931852	7.15974869122345	7.72664796576491
C	2.36604564959528	6.72923678886074	10.07123637538052
N	2.28630309964273	7.36879211355127	11.23746406770297
C	2.42768615000200	7.63777322007322	8.86735135581201
C	2.36782298014667	5.33550621180191	10.04108922700215
H	2.43344566636186	4.82762714223065	9.08099971263708
C	2.41652408495427	9.93965359946345	8.19481797524219
C	3.66115699487795	10.44973312607613	7.74386119658554
C	3.65745590008841	11.44774896277363	6.76402169414099
H	4.60630498478439	11.84092805594129	6.39782836610570
C	1.19737486163543	10.43029255257225	7.66118826512409
C	2.46601046472023	11.93949017104832	6.23502192657266
H	2.48592180770540	12.71453035229529	5.46869064237563
C	4.98195897101354	9.89695296711356	8.25899202845164
H	4.75207628271349	9.26732298454427	9.12951988732885
C	2.28150217364193	4.65006812418908	11.25712792074476
H	2.28210112141284	3.56030874227709	11.26524654630964
C	1.25021253870301	11.42894804570031	6.68279186053689
H	0.32162009882248	11.80791943876959	6.25496378642839
C	-0.14583704249735	9.85507896383943	8.08592108596818
H	0.03374051283601	9.23551670019106	8.97550440256953
C	-0.71150880856293	8.93211462583067	6.98926279629149
H	-0.93323679920257	9.50145165058959	6.07539262184538
H	-1.64496300242805	8.45934816901590	7.32634331615450
H	0.00490052632155	8.14301847866838	6.73116652327953
C	2.12782600960846	13.48667990041643	11.45352874628808
C	-1.16554643441060	10.93677099008226	8.47627088417596
H	-1.43033535294936	11.57608525934180	7.62298485395488
H	-0.77846606278369	11.58278748121436	9.27509284236982
H	-2.09385962577560	10.47195853493697	8.83598081312856
C	5.94834117793622	10.99557943259823	8.72895309537430
H	6.26221840091116	11.64578169070820	7.90085907879157
H	6.85679384099231	10.54614056357563	9.15318455210770
H	5.49045056557686	11.62821537451842	9.50048861930046
C	5.64337838388981	8.99425862993933	7.19973700084857
H	5.92026638568168	9.57530600197463	6.30853825343859
H	4.96239421827217	8.19408499664357	6.88607464559785
H	6.55889416704161	8.53650370984160	7.60066415367671
O	2.70748802257815	11.20594371437227	11.15434154582643
O	1.72116425692174	12.04190873579811	11.58627195650675
N	2.03283802607148	8.97917970319247	13.23107427119847
O	1.99545904314591	7.20350255770985	14.74488192568144
C	2.18979666892124	6.74674211201487	12.41176825095725
C	2.07174097218311	7.66976031653235	13.59989564995329
C	2.18779903163791	5.35333297317158	12.46222689268801
H	2.11089214157214	4.85978062264100	13.42887419647493
C	1.93943641616961	9.98550527811923	14.21724834038158
C	0.67385927366910	10.58739470398748	14.47102231678164
C	0.59938969301175	11.61349931072999	15.41802407057594
H	-0.36272385726046	12.07834750277461	15.63105676654006
C	3.09624902531735	10.40814971118868	14.92430021765393
C	1.73195662378753	12.04232046787639	16.10721554593019
H	1.65339745840530	12.84103888569981	16.84506487767328
C	-0.58244494002567	10.05690285891844	13.79831486823259
H	-0.26863909331075	9.59853434198181	12.84903827619908
C	2.96379333801781	11.43740342885299	15.86095982350712

H	3.84084156587542	11.76698068660345	16.41903854700335
C	4.44998977304604	9.74358520602403	14.72157799285748
H	4.34930706680145	9.04598137956081	13.87947631838609
C	4.84350871613956	8.91870409642588	15.96169871809662
H	4.98911886911692	9.56806822837266	16.83661931297799
H	5.78617747952404	8.38284184595427	15.78190551590297
H	4.06655373710618	8.18393300799640	16.20278032320752
C	5.55419895571474	10.74834163380401	14.35370940837204
H	5.72628500303747	11.47602322383682	15.15874872946702
H	5.30222677990634	11.30619705614319	13.44302623160589
H	6.50278015888949	10.22233920383914	14.17850500799813
C	-1.62437671274980	11.13506760240173	13.47313649495692
H	-2.06408560722180	11.57051711186667	14.38101335633692
H	-2.44953520670235	10.69467161955254	12.89730609297803
H	-1.19335737392273	11.94967717958833	12.87844402274489
C	-1.21135004638158	8.94121367268649	14.65939414448874
H	-1.57975482636917	9.35387038314894	15.60942270407305
H	-0.48478913838241	8.15495715615001	14.89569075565781
H	-2.06338540712766	8.48557627355322	14.13514111423255

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