

Supporting Information:

Coordination Chemistry and Reactivity of Cupric-hydroperoxide Species Featuring a Proximal H-bonding Substituent

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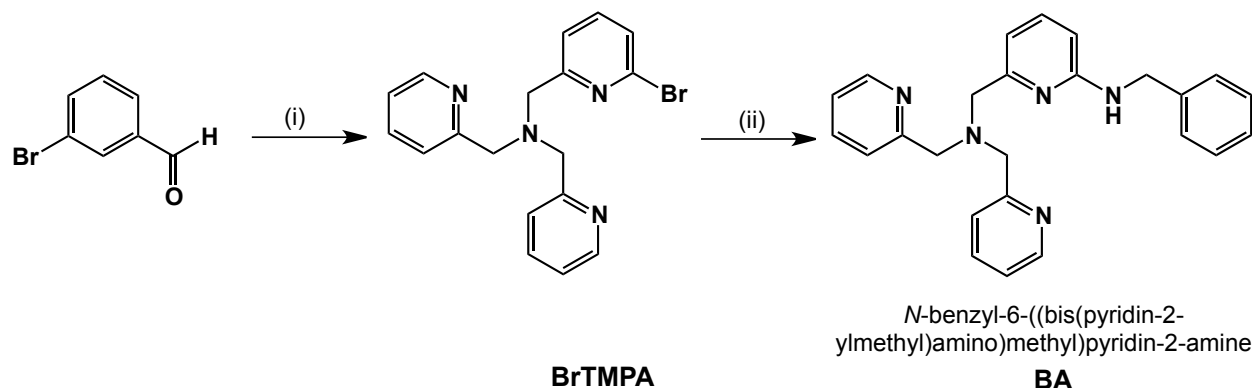
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1. Materials and methods.

General. All materials used were commercially available analytical grade from Sigma-Aldrich chemicals and TCI. Acetone was distilled under an inert atmosphere over CaSO_4 and degassed under argon prior to use. Diethyl ether was used after being passed through a 60 cm long column of activated alumina (Innovative Technologies) under argon. Tetrahydrofuran (THF) was distilled under an inert atmosphere from Na/benzophenone and degassed with argon prior to use. Pentane was freshly distilled from calcium hydride under an inert atmosphere and degassed prior to use. $\text{Cu}(\text{CH}_3\text{CN})_4(\text{B}(\text{C}_6\text{F}_5)_4)$ were synthesized according to literature protocols, and their identity and purity were verified by elemental analysis and/or ^1H -NMR.^{1,2} Synthesis and manipulations of copper salts were performed according to standard Schlenk techniques or in an MBraun glovebox (with O_2 and H_2O levels below 1 ppm).

Instrumentation. UV-Vis spectra were recorded with an HP Model 8453A diode array spectrophotometer equipped with a liquid nitrogen chilled Unisoku USP-203-A cryostat. NMR spectroscopy was performed on Bruker 300 and 400 MHz instruments with spectra calibrated to either internal tetramethylsilane (TMS) standard or to a residual protio solvent. EPR measurements were performed on an X-Band Bruker EMX CW EPR controlled with a Bruker ER 041 XG microwave bridge operating at the X-band (~9 GHz). ESI-Mass spectra were acquired using a Finnigan LCQDeca ion-trap mass spectrometer equipped with an electrospray ionization source (Thermo Finnigan, San Jose, CA).

2. Ligand synthetic scheme.



3. Synthesis of ligands.

(i) 1-(6-bromopyridin-2-yl)-*N,N*-bis(pyridin-2-ylmethyl)methanamine (BrTMPA). 6-Bromo-2-pyridinecarboxaldehyde (5 g, 26.88 mmol) and di-(2-picolyl)amine (4.89 g, 24.54 mmol) were dissolved in 100 mL of 1,2-dichloroethane in 250 mL two-neck-flask and sodium triacetoxymethylborohydride (8.32 g, 39.26 mmol) was added into the solution. The solution mixture was stirred for 2 days under Ar. The solvent was removed by high vacuum rotary evaporation. The resulting crude product was dissolved in 100 mL of CH₂Cl₂, washed two times with saturated Na₂CO₃ solution. After drying over MgSO₄, the solution was filtered and removed by rotary evaporation. The resulting yellow oil was purified by column chromatography (alumina, 100 % ethylacetate, *R_f* = 0.7) yielding 8.78 g of a yellowish white solid (97 % yield).

¹H-NMR (400 MHz, CDCl₃): δ 8.6 (d, 2H), 7.7–7.4 (m, 6H), 7.3–7.1 (m, 3H), 3.87 (Br s, 6H).

ESI-MS, *m/z*: 391.4 (M + Na), 369.5 (M + H⁺).

(ii) *N*-benzyl-6-((bis(pyridin-2-ylmethyl)amino)methyl)pyridin-2-amine (BA). BrTMPA (2.1 g, 5.687 mmol) and benzylamine (6 g, 56.00 mmol) were placed in a high pressure tube (Ace pressure tube, Aldrich Z18, 106-111) and dissolved in 3 mL toluene/12 mL water with 0.1 g NaOH. The resulting mixture was stirred at 160 °C for 7 days and then cooled to room temperature. The solution obtained was extracted with CH₂Cl₂ several times. The combined organic layers were dried with MgSO₄, filtered, and the volatile components were removed by rotary evaporation yielding a pale yellow oil. The resulting yellow oil was purified by a column chromatography (Alumina, 50 % ethylacetate with hexane, *R_f* = 0.57). The product fraction was collected and the solvent was removed under reduced pressure to afford the pale yellow oil, BA (1.02 g 45 % yield).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.54 (d, 2H), 7.65 (d, 4H), 7.42-7.26 (m, 6H), 7.13 (t, 2H), 6.86 (d, 1H), 6.25 (d, 1H), 4.49 (s, 2H, $2\text{CH}_2\text{Ph}$), 3.90 (s, 4H, $2\text{CH}_2\text{Py}$), 3.70 (s, 2H, CH_2Py).

ESI-MS, m/z : 418.3 ($\text{L} + \text{Na}$), 396.3 ($\text{L} + \text{H}^+$).

4. Synthesis of the copper (I)/(II) complexes.

$[\text{BACu}^{\text{II}}(\text{CH}_3\text{COCH}_3)](\text{ClO}_4)_2$. In a 100 mL Schlenk flask, 200 mg (0.506 mmol) of BA ligand was dissolved in 10 mL dry acetone. 187 mg (0.506 mmol) of $\text{Cu}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 mL dry acetone and then copper solution was added to BA solution. After stirring for 10 min at room temperature, the complex was precipitated as blue solid upon addition of diethyl ether (100 mL). The supernatant was decanted and the resulting blue solid was washed two times with diethyl ether and dried under vacuum to afford 179 mg of a copper(II) complex (50 % yield). Single crystals were obtained by vapor diffusion of diethyl ether into a solution of the complex in acetone.

Elemental analysis: ($\text{C}_{25}\text{H}_{27}\text{Cl}_2\text{CuN}_5\text{O}_9$) Calculated: C (44.42), H (4.03), N (10.36); found: C (44.48), H (4.77), N (10.18).

EPR spectrum (Figure S1): X-band ($\nu = 9.186$ GHz) spectrometer in acetone at 70 K: $g_{\parallel} = 2.07$, $A_{\perp} = 108$ G, $g_{\perp} = 2.22$.

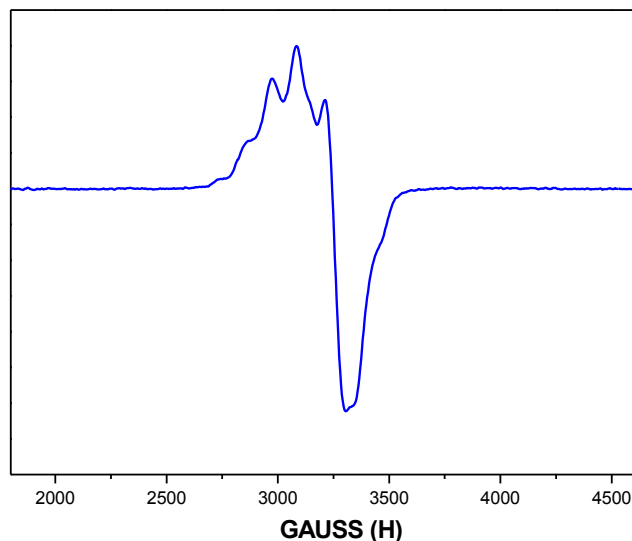


Figure S1. EPR spectrum of $[\text{BACu}^{\text{II}}(\text{CH}_3\text{COCH}_3)]^{2+}$ (**1**) (2 mM) in acetone at 70 K.

$[(\text{BA})\text{Cu}^{\text{I}}](\text{B}(\text{C}_6\text{F}_5)_4)$. In a 100 ml schlenk flask located in the glove box, 172 mg (0.190 mmol) of

[Cu(CH₃CN)₄](B(C₆F₅)₄) was dissolved in 7 ml of THF. 75.2 mg (0.190 mmol) of BA ligand dissolved in approximately 5 ml of THF was added to the copper solution yielding an immediate color change from pale yellow to dark yellow. This dark yellow solution was allowed to stir for 20 min at which time approximately 100 ml of degassed pentane was added to the solution. After 3 hours, the supernatant was decanted and the oil removed from the glove box and dried under vacuum for 20 min affording 182 mg of a bright yellow powder (84 % yield).

¹H-NMR (400 MHz, acetone-d₆): δ 8.4 (s, 3H), 7.75 (s, 2H), 7.6-7.30 (m, 11H), 5.02 (s, 4H, 2CH₂Ph), 3.76 (m, 2H, CH₂Py), 1.92 (t, 2H, CH₂Ph).

Elemental analysis: (C₄₉H₂₅BCuF₂₀N₅) Calculated: C (51.71), H (2.21), N (6.15); found: C (51.18), H (2.18), N (5.65).

5. X-ray crystallography.

All reflection intensities were measured at 110(2) K using a KM4/Xcalibur (detector: Sapphire3) with enhance graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å) under the program CrysAlisPro (Version 1.171.33.55, Oxford Diffraction Ltd., 2010). The program CrysAlisPro (Version 1.171.33.55, Oxford Diffraction Ltd., 2010) was used to refine the cell dimensions. Data reduction was done using the program CrysAlisPro (Version 1.171.33.55, Oxford Diffraction Ltd., 2010). The structure was solved with the program SHELXS-97³ and was refined on *F*² with SHELXL-97⁴. Analytical numeric absorption corrections based on a multifaceted crystal model were applied using CrysAlisPro (Version 1.171.33.55, Oxford Diffraction Ltd., 2010). The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H-atoms were placed at calculated positions (except for those attached to N5A and N5B) using the instructions AFIX 23, AFIX 43, or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times *U*_{eq} of the attached C atoms. The positions and the isotropic temperature factors of the H atoms located on N5A and N5B (*i.e.*, H5A and H5B, respectively) were refined freely. The distances N5A–H5A and N5B–H5B were restrained to be 0.88(3) Å using the DFIX instruction.

The asymmetric contains two crystallographically independent Cu^{II} complexes and four perchlorate counterions. The structure of x0676a is mostly ordered. Three of the four perchlorate counterions are found to be disordered over two orientations. The occupancy factors for the major components of the disorder refine to 0.795(4), 0.882(4) and 0.726(15). A first refinement against *F*² was not satisfactory because some residual electron density were found in four voids [located approximately at (0, 0, 0.25), (0.5, 0.51, 0.25), (0, 0.99, 0.75), (0.5, 0.49, 0.75)], which include 24 electrons in a volume of 116 Å³ per void. Each void is probably partially occupied by some disordered solvent molecules (acetone). The contribution of the disordered solvent molecules was then taken out for the subsequent stages of the

refinement using the program SQUEEZE.⁴ [(BA)Cu^{II}(CH₃COCH₃)](ClO₄)₂, Fw = 716.02*, green block, 0.32 × 0.22 × 0.10 mm³, monoclinic, C2/c (no. 15), *a* = 37.8351(6), *b* = 10.91546(16), *c* = 30.7221(5) Å, β = 98.8288(15)°, *V* = 12537.5(3) Å³, *Z* = 16, *D*_x = 1.517 g cm⁻³*, μ = 0.928 mm⁻¹*, abs. corr. range: 0.807–0.923. 49626 Reflections were measured up to a resolution of (sin θ/λ)_{max} = 0.62 Å⁻¹. 12310 Reflections were unique (*R*_{int} = 0.0436), of which 8309 were observed [*I* > 2 σ (*I*)]. 931 Parameters were refined using 434 restraints. *R*₁/*wR*₂ [*I* > 2 σ (*I*)]: 0.0357/0.0830. *R*₁/*wR*₂ [all refl.]: 0.0625/0.0882. *S* = 0.942. Residual electron density found between −0.49 and 0.52 e Å⁻³.

* excluding the disordered solvent contribution.

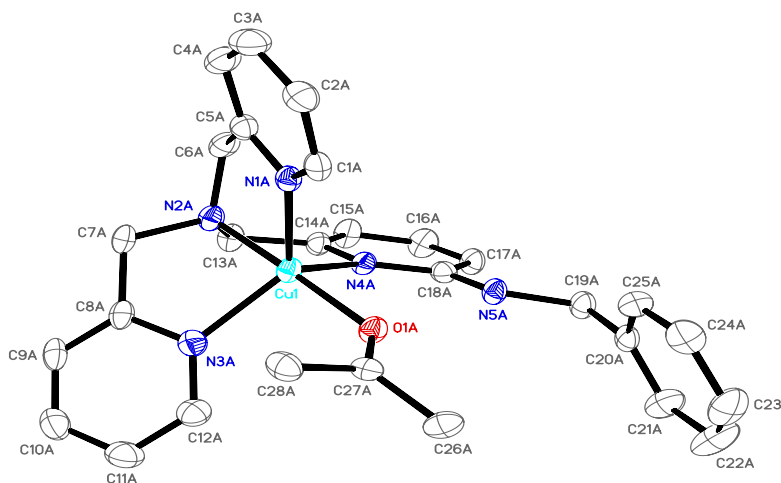


Figure S2. Displacement ellipsoid plot (50 % probability level) of the cationic complex, [BACu^{II}(CH₃COCH₃)]²⁺. The second crystallographic cationic complex and the H-atoms were removed for clarity.

Table S1. Selected bond distances and bond angles for [(BA)Cu^{II}(CH₃COCH₃)](ClO₄)₂ complex.

Bond Lengths (Å)	
Cu1-O1A	1.982(5)
Cu1-N1A	2.029(2)
Cu1-N2A	1.996(2)
Cu1-N3A	2.058(2)
Cu1-N4A	2.150(2)
Bond Angles (°)	
O1A-Cu1-N1A	100.07(7)
O1A-Cu1-N2A	176.61(8)
O1A-Cu1-N3A	96.25(8)

O1A-Cu1-N4A	96.40(7)
N1A-Cu1-N4A	113.69(8)
N2A-Cu1-N1A	83.23(8)
N2A-Cu1-N3A	82.30(8)
N2A-Cu1-N4A	81.46(8)
N3A-Cu1-N1A	126.67(8)
N3A-Cu1-N4A	114.37(8)

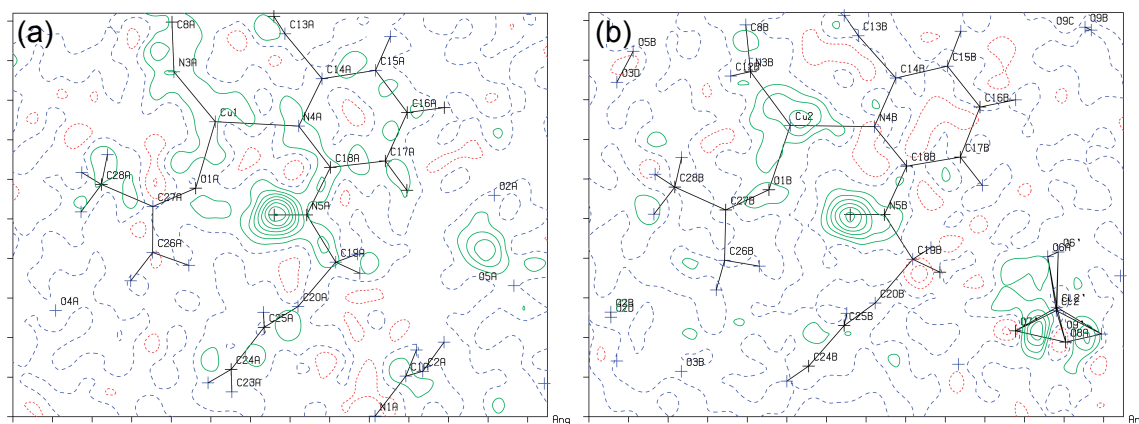


Figure S3. The contoured residual difference Fourier maps of molecules A and B with respect to the plane defined by the atomic coordinates of atoms N5n, H_5n, and O1n (n = A,B). Prior to the difference Fourier map calculations, the H atoms attached to the N atoms were omitted so that their positions are derived by locating the residual electron density (see green circles densely packed). (a) N5A_O1A, (b) N5B_O1B.

6. DFT Calculations

The calculations were performed with ORCA 2.9.0 program.⁵ The geometry of $[\text{BA-Cu}^{\text{II}}\text{-OOH}]^+$ was fully optimized starting from the X-ray crystal structure coordinates of $[\text{BA-Cu}^{\text{II}}(\text{Acetone})]^{2+}$. A DFT spin-unrestricted formalism has been used and the Becke88⁶ exchange and Perdew86⁷ correlation nonlocal functionals were used as implemented in ORCA (BP86) as well as the Becke's three-parameter hybrid functional with the correlation functional of Lee, Yang, and Parr (B3LYP)⁸ for geometry optimization of the BA-Cu(II)-OOH species. Frequency calculations were performed with the B3LYP functional. The def-2-SVP basis set present in ORCA was used for all atoms except oxygen, copper, and nitrogen for which the def-2-TZVP basis set has been used as implemented in ORCA. Van der Waals

forces were considered in the calculations⁹ and the COSMO model¹⁰ implemented in ORCA has been adopted to take into account of solvent effects where a dielectric constant of 20.7 was used for the acetone solvent and 6.97 was adopted for 2-MeTHF.

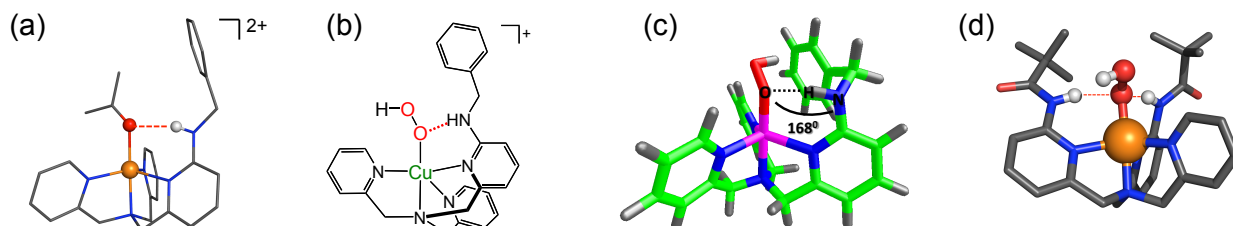


Figure S4. (a) The crystal structure of $[(BA)Cu^{II}(Acetone)]^{2+}$, (b) $[(BA)Cu^{II}-OOH]^+$ species, (c) Peroxo Opt_BP86 in acetone and (d) $[(bppa)Cu^{II}-OOH]^+$.

Table S2. Selected bond distances and bond angles for the crystal structure of $[BACu^{II}(Acetone)]^{2+}$ (Cu-Acetone), the optimized structure of $[BACu^{II}-OOH]^+$ calculated with the BP86 DFT functional in acetone and MeTHF (Peroxo Opt_BP86) and with the B3LYP DFT functional (Peroxo Opt_B3LYP) in this work, as well as the crystal structure of $[(bppa)Cu^{II}-OOH]^+$ determined by Masuda and co-workers.

	N-H (Å)	H...O (Å)	N...O (Å)	N-H-O (°)
Crystal (Cu-Acetone)	--	--	2.981(3), 2.886(3)	163(3), 161(3)
Peroxo Opt_BP86 (Acetone)	1.04(2)	1.77(2)	2.80(2)	168(2)
Peroxo Opt_B3LYP (Acetone)	1.03(2)	1.82(2)	2.83(2)	167(2)
Crystal* [(bppa)Cu^{II}-OOH]⁺	0.92, 0.89	1.93, 1.90	2.78, 2.79	162, 164
Peroxo Opt_BP86 (MeTHF)	1.04(2)	1.77(2)	2.80(2)	168(2)
Peroxo Opt_B3LYP (MeTHF)	1.02(2)	1.78(2)	2.79(2)	165(2)

* Wada, A.; Harata, M.; Hasegawa, K.; Jitsukawa, K.; Masuda, H.; Mukai, M.; Kitagawa, T.; Einaga, H. *Angew. Chem. Int. Ed.* 1998, 37, 798-799.

Calculated Geometries**[BA-Cu^{II}-OOH]⁺, BP86 Functional, Acetone Solvent**

Cu	11.281106	3.410452	2.271647
C	8.279753	3.894437	2.767696
H	8.652667	4.481807	3.618050
C	6.911996	3.726341	2.514812
H	6.172326	4.187641	3.184090
C	6.520801	2.971538	1.399612
H	5.456074	2.822647	1.166023
C	7.512922	2.390307	0.592808
H	7.249160	1.770590	-0.276462
C	8.859976	2.597350	0.917357
C	9.997678	2.006967	0.116792
H	9.671234	1.114023	-0.457365
H	10.347533	2.762551	-0.617586
C	10.896446	0.551061	1.907071
H	11.070409	-0.414204	1.386078
H	9.829041	0.573625	2.209012
C	11.741454	0.670881	3.157618
C	12.213595	-0.436344	3.876290
H	12.022182	-1.454523	3.507185
C	12.926893	-0.215978	5.066417
H	13.308455	-1.067525	5.649489
C	13.149974	1.102269	5.497163
H	13.703995	1.317009	6.422115
C	12.656057	2.154833	4.714761
H	12.792771	3.213900	4.981227
C	12.431504	1.616611	0.303754
H	12.395578	0.871458	-0.518834
H	13.184389	1.271453	1.041573
C	12.825885	2.982381	-0.202143
C	13.338908	3.188649	-1.482430

H	13.475700	2.340919	-2.167989
C	13.657598	4.509848	-1.867036
H	14.067121	4.713474	-2.867939
C	13.456381	5.554042	-0.970582
H	13.715624	6.587461	-1.238553
C	12.930567	5.270069	0.321012
C	12.030681	7.490054	0.931672
H	12.339009	7.834691	-0.074137
H	12.324561	8.280198	1.649600
C	10.527940	7.255287	0.987204
C	9.737949	7.855859	1.992581
H	10.203795	8.563052	2.698563
C	8.356860	7.583003	2.082302
H	7.755248	8.063222	2.869117
C	7.755624	6.697560	1.173364
H	6.680360	6.476694	1.244974
C	8.536301	6.086541	0.173517
H	8.071053	5.382155	-0.533215
C	9.908401	6.362220	0.081760
H	10.507955	5.879804	-0.705514
O	10.528769	5.574251	4.040634
N	9.228585	3.354918	1.981366
N	11.134897	1.705291	1.012523
N	11.973296	1.936564	3.577382
N	12.606831	3.997312	0.676092
N	12.750513	6.248601	1.272815
H	12.398999	5.839689	2.163527
O	11.662314	4.889398	3.466377
H	10.281207	6.223917	3.331462

[BA-Cu^{II}-OOH]⁺, B3LYP Functional, Acetone Solvent

Cu	11.300735	3.372583	2.285811
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C	8.209834	3.846670	2.659236
H	8.534588	4.466446	3.494189
C	6.860492	3.653148	2.365785
H	6.096755	4.131389	2.981395
C	6.521646	2.843876	1.280388
H	5.475440	2.668839	1.018652
C	7.544559	2.245616	0.539353
H	7.321567	1.590437	-0.305076
C	8.869793	2.489554	0.899991
C	10.033184	1.900161	0.138835
H	9.740644	0.976201	-0.385944
H	10.350467	2.623043	-0.628463
C	10.984857	0.500021	1.921937
H	11.209606	-0.440056	1.392467
H	9.922562	0.467055	2.208722
C	11.804047	0.633417	3.184996
C	12.288510	-0.463671	3.897902
H	12.132001	-1.475862	3.519552
C	12.970697	-0.235885	5.096721
H	13.360429	-1.076616	5.675672
C	13.151585	1.077099	5.541271
H	13.679730	1.295457	6.471214
C	12.646616	2.117918	4.762533
H	12.754542	3.169016	5.038912
C	12.467936	1.616631	0.317386
H	12.441479	0.864334	-0.487286
H	13.238072	1.309487	1.041037
C	12.815588	2.982706	-0.217704
C	13.308973	3.178277	-1.497915
H	13.463612	2.331178	-2.167567
C	13.585382	4.497133	-1.903134
H	13.976514	4.693681	-2.904441
C	13.367935	5.545708	-1.027607
H	13.598790	6.571763	-1.314813

C	12.867307	5.269729	0.269978
C	12.025734	7.519524	0.888395
H	12.310318	7.838563	-0.123350
H	12.386929	8.290645	1.584206
C	10.518576	7.372764	1.004392
C	9.817752	7.962827	2.068828
H	10.353075	8.597772	2.781373
C	8.438534	7.753504	2.221519
H	7.907802	8.220437	3.055351
C	7.748848	6.945490	1.313141
H	6.676892	6.772592	1.435223
C	8.439582	6.352897	0.247661
H	7.905581	5.715414	-0.462020
C	9.811092	6.565914	0.094464
H	10.341703	6.097014	-0.738658
O	10.505457	5.434739	4.058446
N	9.187299	3.286842	1.937618
N	11.178993	1.671737	1.041454
N	11.993866	1.889964	3.619061
N	12.581910	4.002237	0.638368
N	12.688487	6.248369	1.211621
H	12.365742	5.860911	2.104961
O	11.668484	4.846192	3.444530
H	10.255765	6.135469	3.426135

[BA-Cu^{II}-OOH]⁺, BP86 Functional, 2-MeTHF Solvent

Cu	11.260530	3.381268	2.243828
C	8.253839	3.868876	2.655444
H	8.611936	4.482861	3.493525
C	6.891395	3.689753	2.382057
H	6.138885	4.166992	3.025342
C	6.522721	2.902616	1.281730
H	5.462981	2.743171	1.032760

C	7.531310	2.302659	0.509463
H	7.284415	1.659698	-0.347936
C	8.871867	2.522712	0.852605
C	10.025531	1.920791	0.082600
H	9.712212	1.011129	-0.473126
H	10.377293	2.660092	-0.667260
C	10.928773	0.506223	1.902065
H	11.123644	-0.463632	1.396306
H	9.857972	0.516412	2.193238
C	11.758669	0.656095	3.160425
C	12.247059	-0.433318	3.895125
H	12.081217	-1.459364	3.535316
C	12.943295	-0.185429	5.090085
H	13.337302	-1.022507	5.685689
C	13.132622	1.141579	5.509244
H	13.671925	1.377940	6.437593
C	12.623797	2.175363	4.711335
H	12.732832	3.240204	4.967699
C	12.463423	1.586782	0.304673
H	12.457241	0.832339	-0.510708
H	13.214134	1.268416	1.056566
C	12.830289	2.957556	-0.210899
C	13.332294	3.168043	-1.494742
H	13.484895	2.320959	-2.177721
C	13.619609	4.495023	-1.886324
H	14.017004	4.703345	-2.891153
C	13.405573	5.538289	-0.992371
H	13.645429	6.574495	-1.267149
C	12.899343	5.249034	0.306990
C	12.047146	7.486435	0.947912
H	12.336029	7.822361	-0.066758
H	12.393873	8.263499	1.656760
C	10.538895	7.310818	1.050298
C	9.800417	7.963032	2.062125

H	10.312065	8.664408	2.741234
C	8.413729	7.741586	2.197435
H	7.852770	8.261260	2.989144
C	7.756566	6.855179	1.329506
H	6.677191	6.671839	1.438724
C	8.486272	6.193438	0.323333
H	7.977029	5.486019	-0.349400
C	9.863232	6.418243	0.185480
H	10.424519	5.892547	-0.602458
O	10.465516	5.540392	4.001156
N	9.218526	3.309217	1.902789
N	11.155919	1.652613	0.995959
N	11.958462	1.930553	3.569031
N	12.595648	3.970687	0.664413
N	12.723421	6.217612	1.263948
H	12.376052	5.808971	2.156372
O	11.609288	4.863659	3.445719
H	10.269081	6.237465	3.321663

[BA-Cu^{II}-OOH]⁺, B3LYP Functional, 2-MeTHF Solvent

Cu	11.175553	3.164013	2.091226
C	8.046610	3.464643	1.991748
H	8.224471	4.187705	2.787208
C	6.760683	3.150325	1.554712
H	5.896924	3.643493	2.004265
C	6.612819	2.190489	0.550651
H	5.621020	1.910872	0.187384
C	7.754851	1.582254	0.024496
H	7.680211	0.818781	-0.752582
C	9.007682	1.965246	0.506906
C	10.290763	1.405703	-0.062322
H	10.130051	0.408251	-0.503490

H	10.618846	2.069430	-0.876832
C	11.215839	0.250217	1.896540
H	11.606538	-0.684897	1.462376
H	10.139820	0.102027	2.078151
C	11.871297	0.559800	3.222963
C	12.406758	-0.421824	4.057090
H	12.419864	-1.465988	3.737884
C	12.919371	-0.038578	5.300250
H	13.344025	-0.786863	5.973841
C	12.886532	1.309858	5.666518
H	13.278078	1.648289	6.627537
C	12.346661	2.230120	4.768456
H	12.296373	3.301224	4.975652
C	12.711135	1.457809	0.359155
H	12.864949	0.660632	-0.386444
H	13.437491	1.304457	1.171882
C	12.927843	2.825667	-0.243725
C	13.535908	3.014079	-1.475781
H	13.886929	2.161934	-2.059160
C	13.670650	4.334949	-1.944941
H	14.147825	4.526953	-2.909379
C	13.205641	5.393880	-1.185842
H	13.326278	6.423034	-1.524422
C	12.593192	5.124035	0.067708
C	11.720173	7.430670	0.516159
H	11.552907	7.471804	-0.572232
H	12.501447	8.171724	0.755544
C	10.433215	7.772480	1.244085
C	10.364674	8.838491	2.150018
H	11.246620	9.463369	2.316775
C	9.181049	9.102089	2.852902
H	9.144892	9.934401	3.560636
C	8.054299	8.296993	2.660790
H	7.133314	8.497943	3.213933

C	8.112483	7.226955	1.755939
H	7.235466	6.593603	1.598198
C	9.293789	6.967689	1.054245
H	9.340881	6.124266	0.359144
O	10.050962	5.133394	3.796517
N	9.140650	2.892920	1.472686
N	11.358443	1.381216	0.956431
N	11.856014	1.852876	3.584100
N	12.459711	3.846147	0.502289
N	12.123824	6.083182	0.892181
H	11.790521	5.743912	1.800092
O	11.290889	4.733001	3.181962
H	9.759198	5.867158	3.224626

7. Titration data monitoring the formation of $\text{BACu}^{\text{II}}\text{-OOH}$ species.

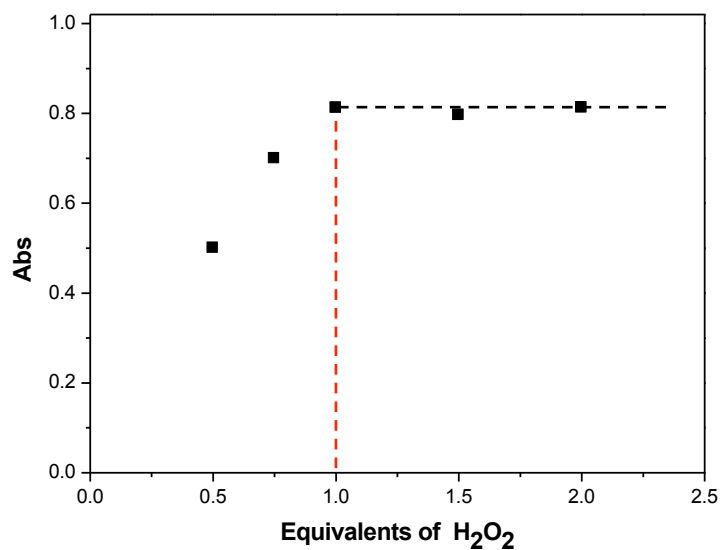


Figure S5. Titration data monitoring the formation of BACu-OOH species (0.55 mM) at 393 nm, showing the completion of reaction upon addition of 1 equiv H_2O_2 .

8. Generation of $\text{Cu}^{\text{II}}\text{-OOH}$ species.

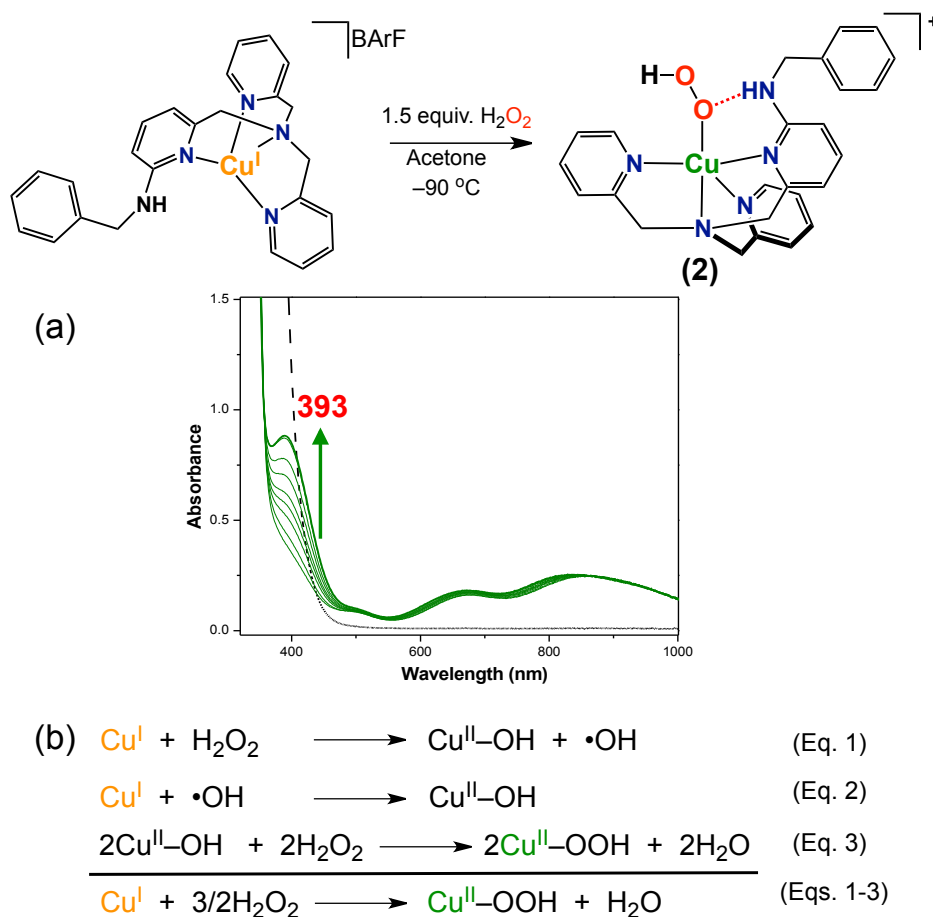


Figure S6. (a) UV-Visible Spectrum of $[(\text{BA})\text{Cu}^{\text{II}}\text{-OOH}]^+$ (**2**) generated from the reaction of the copper(I) complex $[(\text{BA})\text{Cu}^{\text{I}}]\text{B}(\text{C}_6\text{F}_5)_4$ (0.6 mM) (--- dashed) with $3/2$ equiv H_2O_2 in the absence of Et_3N at -90°C in acetone in ~ 40 min, (b) An alternative sequence of reactions (a mechanism) where the more classic first reaction produced is copper(II) + hydroxyl radical ($\cdot\text{OH}$). Also, see the main text for further discussion.

9. Transformation of $[(\text{BA})\text{Cu}^{\text{II}}\text{-OOH}]^+$ (**2**) to a *trans*- μ -1,2-peroxo-dicopper complex $[(\text{BA})\text{Cu}^{\text{II}}]_2(\text{O}_2^{2-})^{2+}$ (**3**)

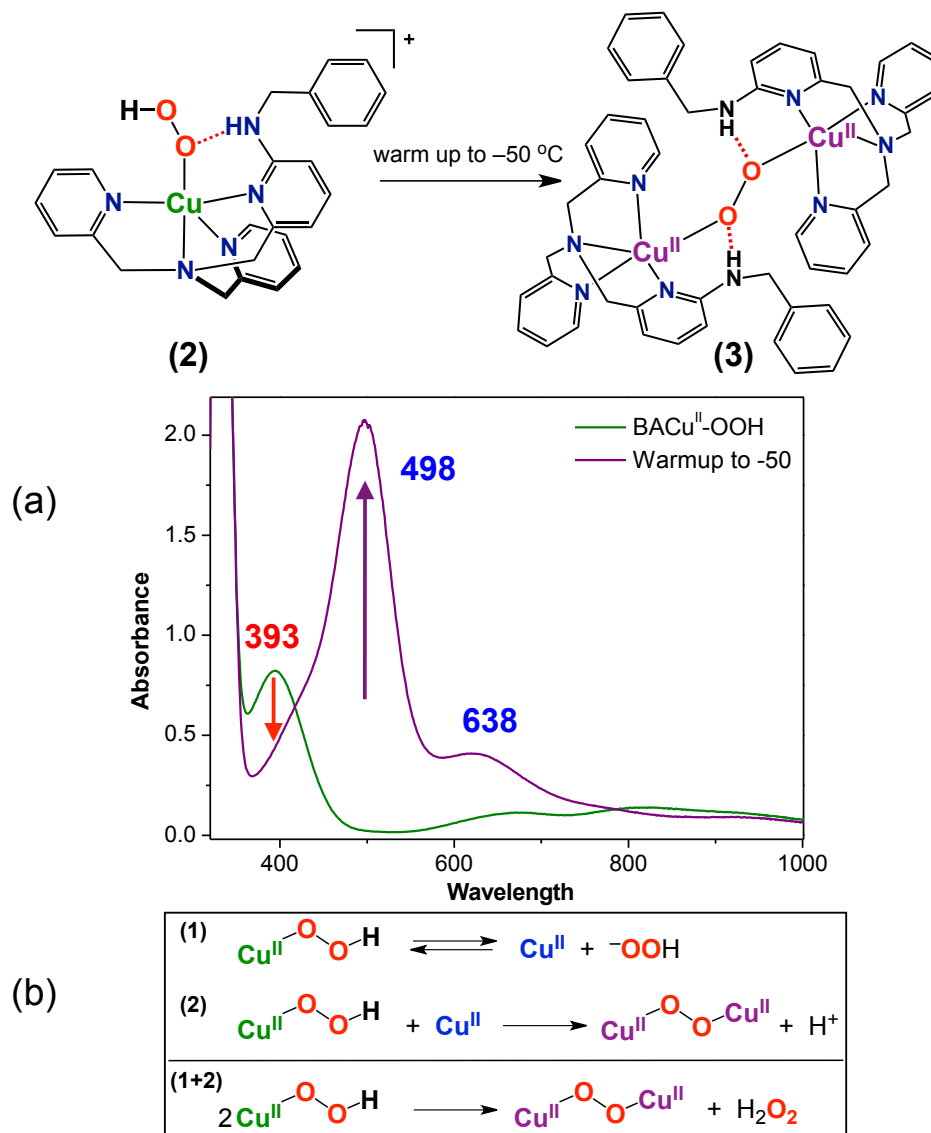


Figure S7. (a) UV-Vis spectra at $-50\text{ }^{\circ}\text{C}$ in acetone, where **2** (0.6 mM, green) transforms to **3** (purple) over 8 hours, (b) the proposed sequence of reactions; $2\text{ (2)} \rightarrow \text{(3)} + \text{H}_2\text{O}_2$.

10. Generation of $[\{(BA)Cu^{II}\}_2(O_2^{2-})]^{2+}$ species.

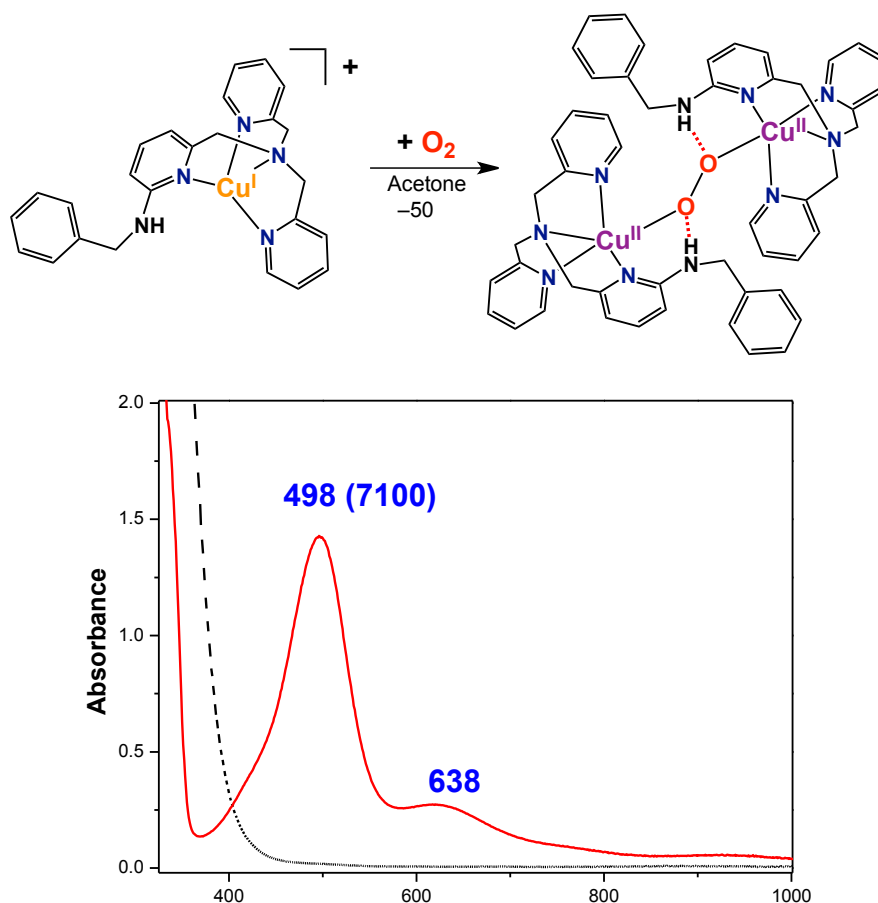
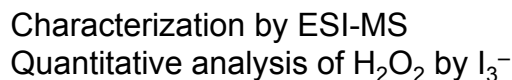


Figure S8. UV-Visible Spectrum of a $trans\text{-}\mu\text{-}1,2\text{-peroxo-dicopper}$ complex $[\{(BA)Cu^{II}\}_2(O_2^{2-})]^{2+}$ (3) by reacting $[(BA)Cu^I]^+$ (0.26 mM) (--- dashed) complex with O_2 in acetone at $-50^\circ C$ in ~ 2 sec.

11. rRaman experimental details

2.5 ml THF of a 0.6 mM solution of $[(BA)Cu^I][B(C_6F_5)_4]$ was transferred to a modified schlenk cuvette, equipped with a rubber septa, The cuvette was sealed with a septum and secured with a plastic zip tie. This cell was transferred to the pre-cooled cryostat and allowed to chill at $-80^\circ C$ with a minimum of 10 minutes allowed for equilibration prior to oxygenation. Oxygenation of the copper samples was achieved by slowly bubbling approximately 5 ml of dioxygen through the solution with a Hamilton gastight syringe equipped with a 3-way valve and needle outlet. After addition of dioxygen, rR measurements were started followed by exposing the sample to a gentle stream of dioxygen, vented out through a needle, for 30 seconds. Dioxygen, $^{16}O_2$ (OX UHP-300 Airgas) and $^{18}O_2$ (Icon 6393), were added to an evacuated Schlenk flask fitted with a septum for the oxygenation reactions described above. Resonance Raman spectra were obtained using Horiba Jobin-Yvon T64000 triple monochromator spectrometer with 1800 gr/mm grating and a liquid nitrogen cooled CCD detector. The spectra were measured in a modified

Scheme S1.



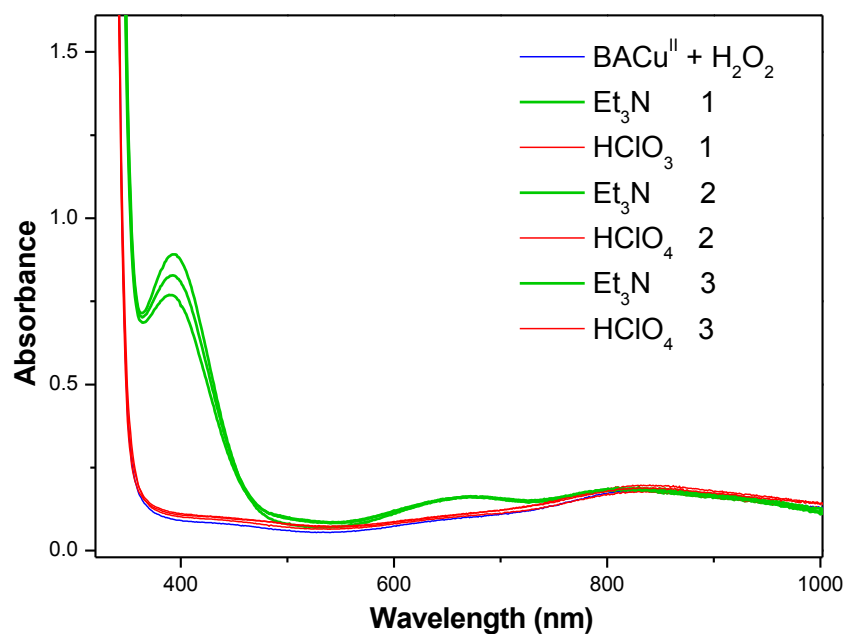


Figure S9. UV-Visible spectrum of reversible acid-base reaction between $[(\text{BA})\text{Cu}^{\text{II}}\text{-OOH}]^+$ (**2**) and $[(\text{BA})\text{Cu}^{\text{II}}]^{2+} + \text{H}_2\text{O}_2$ containing solutions.. Upon addition of HClO_4 (1 equiv = 100 μL , from a stock solution of 0.6 mM $\text{HClO}_4(\text{aq})$) to a solution of 0.6 mM $[(\text{BA})\text{Cu}^{\text{II}}\text{-OOH}]^+$ (**2**) in acetone at -90°C , $[(\text{BA})\text{Cu}^{\text{II}}]^{2+}$ and H_2O_2 are produced. With subsequent addition of one equiv Et_3N (in acetone), species **2** was regenerated. This reversible acid-base reaction was carried out for three cycles showing the recovery of the $\text{Cu}^{\text{II}}\text{-OOH}$ complex **2**.

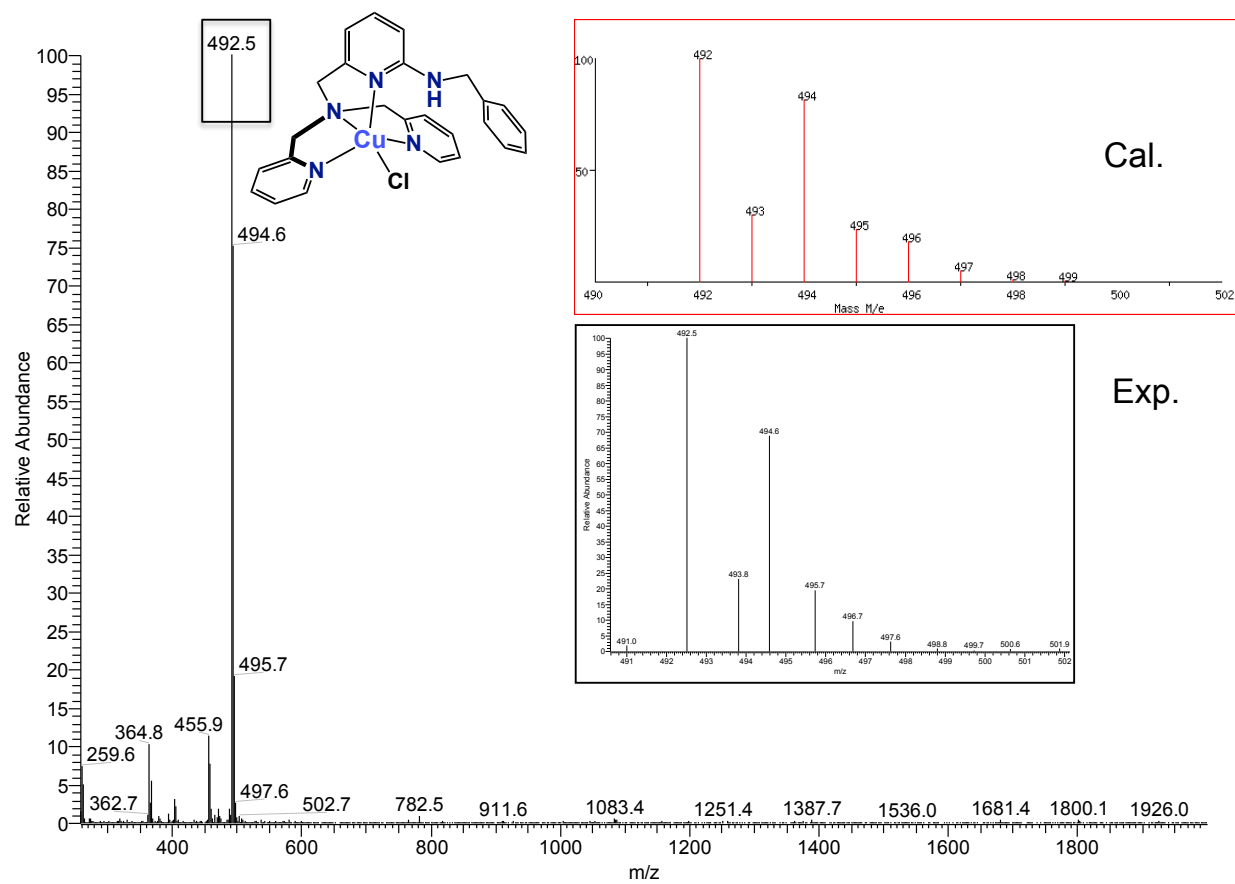


Figure S10. ESI-MS spectrum of $[(BA)Cu^{II}-Cl]^+$

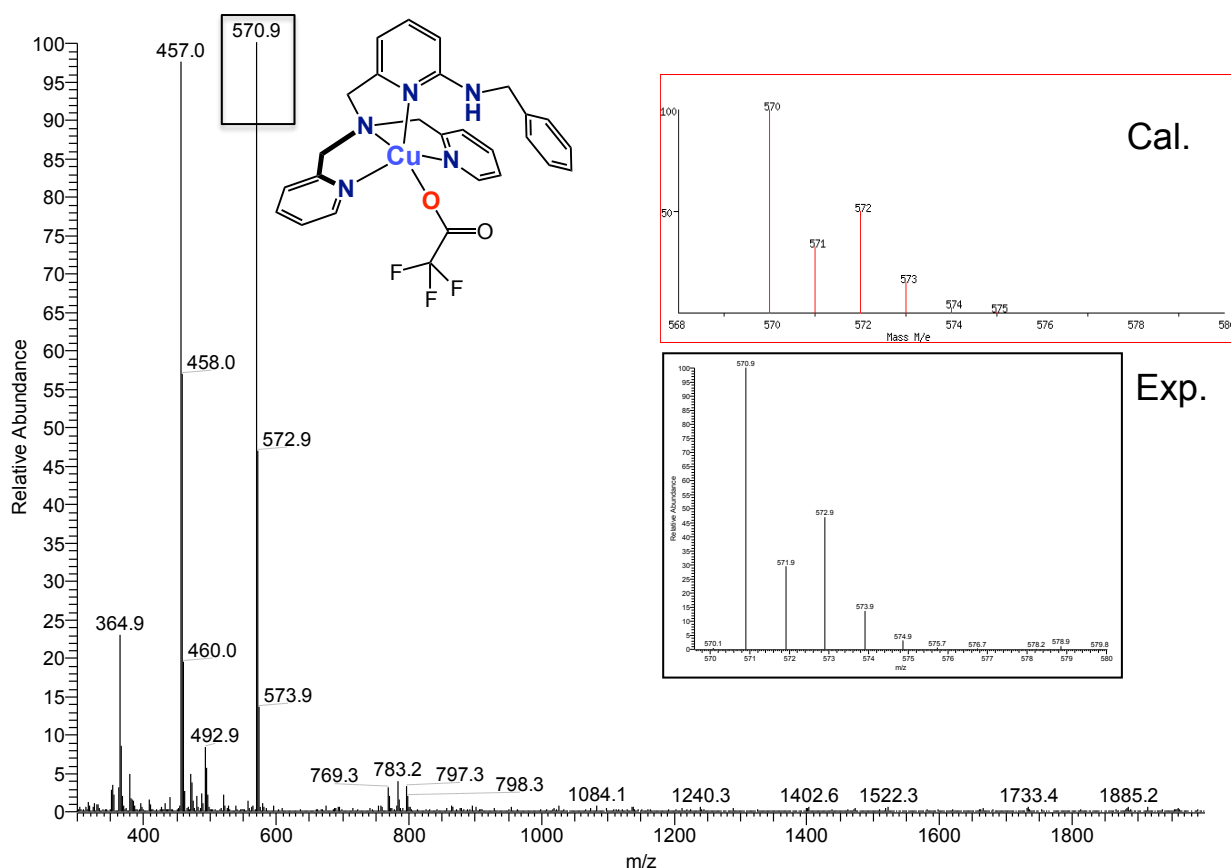


Figure S11. ESI-MS spectrum of $[(BA)Cu^{II}-OOCCF_3]^+$ plus $[(BA)Cu^I]^+$

13. Hydrogen peroxide quantification.

In a typical experiment, a Schlenk cuvette was charged with 2.5 ml of a 0.6 mM solution of $[(BA)Cu^{II}(CH_3OCH_3)](ClO_4)_2$ (**1**) in acetone. $[(BA)Cu^{II}-OOH]^+$ (**2**) was generated at $-90^\circ C$ in acetone by reacting complex **1** with one equiv H_2O_2 (50 % *aq*) in the presence of Et_3N (1 equiv) under Ar. After full formation of **2**, 100 μL (0.6 mM) of stock solution of acid ($HClO_4$, TFA or HCl) was added to release H_2O_2 . To determine the formation of H_2O_2 , 70 μL of solution in the cuvette was taken into 2.0 mL of a CH_3CN saturated NaI solution. This mixture was allowed to incubate for 2 min. The UV-Vis spectrum of this solution was then taken showing the formation of triiodide (I_3^-) at 362 nm compared to that of a standard solution of H_2O_2 . The validity of this procedure was tested with H_2O_2 solutions of known concentrations (**Figure S12 a**).

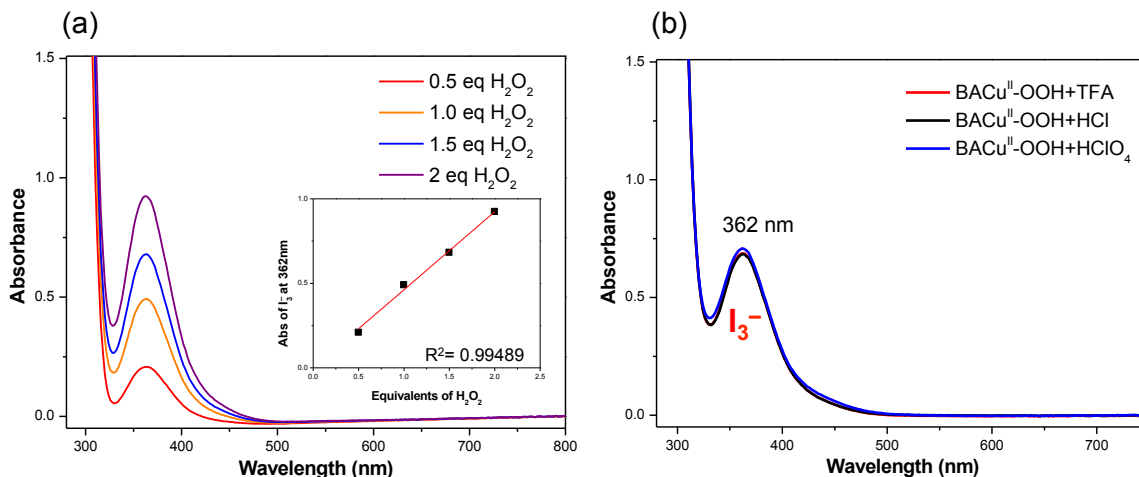


Figure S12. UV-Visible spectrum of triiodide (I_3^-) at 362 nm. (a) Spectrophotometric titration of I_3^- with H_2O_2 solutions (stock solution, 0.6 mM), (b) adding 1 eq acid to the $Cu^{II}-OOH$ species.

14. References.

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