Electronic Supporting Information for:

Encapsulation of synthetic tricopper cluster in a synthetic cryptand enables facile redox processes from $Cu^{I}Cu^{I}Cu^{I}$ to $Cu^{II}Cu^{II}Cu^{II}$ states

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Contents

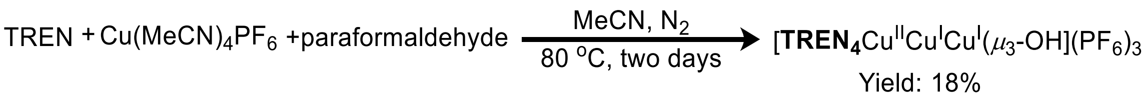
1.Materials and Methods

General: All reactions were carried out under a nitrogen atmosphere in an MBraun glovebox or using Schlenk techniques.

Instrumentation: Nuclear magnetic resonance (NMR) spectra were recorded on DXP 400 MHz (^{1}H: 400 MHz) and AVIII 600 MHz (^{1}H: 600 MHz) at ambient temperature. Chemical shift values for protons were referenced to the residual proton resonance of acetone-d_6 (δ: 2.05 ppm) and tetrahydrofuran-d_8 (THF-d_8, δ: 1.72 ppm and 3.58 ppm). X-ray crystallographic analyses were performed under a cold nitrogen stream (Oxford Cryosystems Cryostream) at 100 K (**4a, 4b, 4c, 4a**-BAr^{F}_4) on a Bruker D8 Venture instrument with Mo Ka radiation source (λ = 0.7107 Å) and a Photon II detector. Elemental analyses were performed by Midwest Micro Lab (Indianapolis, IN, http://midwestlab.com/). ESI mass spectra were recorded on a Bruker MicrOTOF. EPR measurements were performed in 4 mm low-pressure quartz tubes on a Bruker EMXPlus X-band EPR spectrometer equipped with a Coldedge cryostat with small-volume power saturation. Solid-state IR was recorded on a Bruker Alpha II FTIR spectrometer. Cyclic voltammogram was performed using Bio-Logic SAS SP-50 with a glassy carbon working electrode, a platinum wire counter electrode and a Ag/Ag^+ reference electrode (a commercial leakless miniature Ag/AgCl reference is used for aqueous solution and a $Ag/AgNO_3$ (0.01 M) reference electrode is used for organic solution).

Materials: Anhydrous acetone and anhydrous methanol were purchased from Acros and Alfa Aesar, respectively, and were used as received. Dichloromethane, acetonitrile, diethyl ether, tetrahydrofuran, and fluorobenzene were dried and degassed under nitrogen using a Pure Process Technologies (PPT, Nashua, NH) solvent purification system, and stored over 4 Å molecular sieves. Acetone-d_6 (Cambridge Isotope Laboratories, Inc.) was purified by distillation, deoxygenated by three freeze-pump-thaw cycles, and dried over 4 Å molecular sieves prior to use. Tetrahydrofuran-d_8 (Cambridge Isotope Laboratories, Inc.) was deoxygenated by three freeze-pump-thaw cycles and dried over 4 Å molecular sieves prior to use. Tetrakis(acetonitrile)copper(I) hexafluorophosphate (Sigma-Aldrich), paraformaldehyde (Acros), tris(2-aminoethyl) amine (TREN, TCI), cobaltocene (Strem), tetra-n-butylammonium tetrafluoroborate (Sigma-Aldrich), tetra-n-butylammonium chloride (Combi-Blocks), decamethylferrocene (Sigma-Aldrich), silver hexafluorophosphate (Strem), iodine (VWR), sodium iodide (Sigma-Aldrich), triazabicyclodecene (TBD, Sigma-Aldrich), dioxygen (Praxair), and ^{18}O-dioxygen (Sigma-Aldrich) were purchased and used without further purification. Sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate was prepared by a published method.[1] AcOH (glacial, Fisher) and heptane (anhydrous, Alfa Aesar) were deoxygenated by three freeze-pump-thaw cycles before use.

Synthesis and characterization of [TREN$_4$Cu^{I}Cu^{I}Cu^{II}(μ_3-OH)](PF$_6$)$_3$ (4b)



Tetrakis(acetonitrile)copper(I) hexafluorophosphate (93.3 mg, 0.251 mmol), paraformaldehyde (150 mg, 50.0 mmol), and acetonitrile (10 mL) were added to a 20 mL scintillation vial equipped with a septum under nitrogen atmosphere. Tris(2-aminoethyl) amine (TREN, 0.150 mL, 1.00 mmol) was injected with a syringe. Four other vials with the same suspension were prepared in parallel. The five vials were sealed and heated at 80 °C with vigorous stirring for two days, during which the solution turned dark brown. After the reaction, the solution was allowed to cool down and transferred back to the glovebox. The dark brown suspension from five vials was combined and filtered under a nitrogen atmosphere. The brown filtrate was dried under vacuum to afford an orange oil-like residue. Dichloromethane (10 mL) was added to the residue, and the resulting suspension was allowed to sit overnight at room temperature to yield a mixture of a blue solid and a yellow solid, which was collected by filtration and washed with additional dichloromethane (*ca.* 10 mL), and extracted into acetone (15 mL). The acetone solution was filtered, and all volatiles were removed under vacuum to yield a blue solid. The product was rewashed with dichloromethane (*ca.* 10 mL) and dried under vacuum to afford 106.8 mg of **4b** (18% yield). Single crystals of **4b** suitable for X-ray diffraction were obtained by diffusing diethyl ether to an acetone solution of **4b** at –30 °C.
Elemental analysis, Calcd for $C_{36}H_{73}Cu_3F_{18}N_{16}OP_3$ C, 31.52; H, 5.36; N, 16.34. found C, 31.75; H, 5.39; N, 16.06.
Infrared spectrum (ATR), νOH = 3440 cm^{-1} (Fig. 6);
UV-Vis spectrum (acetone, Fig. S1), λ_{max} = 655 nm (800 M^{-1}cm^{-1}), 790 nm (870 M^{-1}cm^{-1});

ESI-MS spectrum (Fig. S2), M/z = 312.2;
EPR spectrum (acetonitrile, 50 K, Fig. S16), g_1 = 2.14, g_2 = 2.25, g_3 = 2.01, A_3 = 146 MHz.

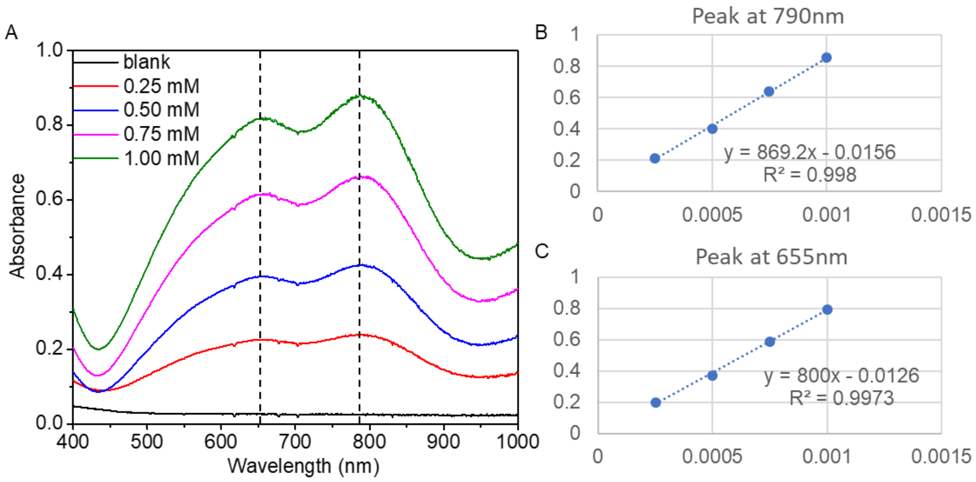


Fig. S1. (A) UV-Vis spectra of [**TREN$_4$**Cu^{I}Cu^{I}Cu^{II}(μ_3-OH)](PF_6)$_3$ (**4b**) at various concentration in acetone at room temperature; Beer's law plots for the peak at 790 nm (B, ε = 870 $M^{-1}cm^{-1}$) and 655 nm (C, ε = 800 $M^{-1}cm^{-1}$).

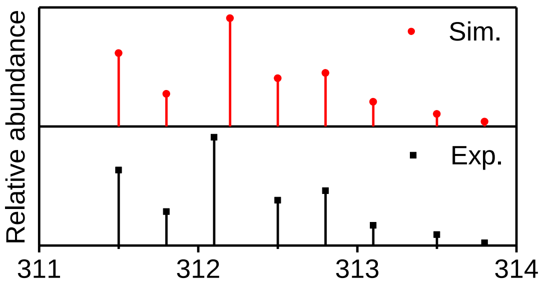
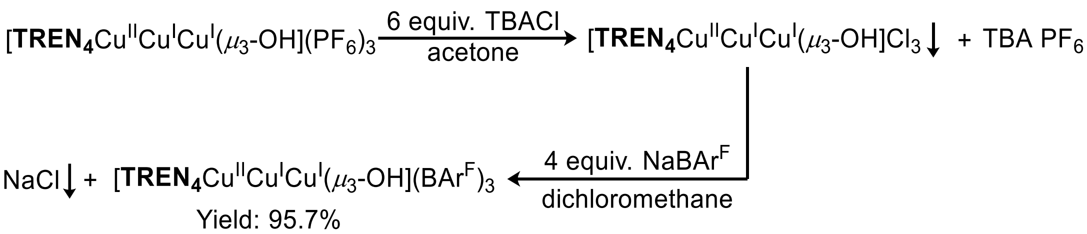


Fig. S2. ESI-MS spectrum (MeCN) and simulation of [**TREN$_4$**Cu^{I}Cu^{I}Cu^{II}(μ_3-OH)](PF_6)$_3$.

Synthesis and characterization of [TREN$_4$Cu^{I}Cu^{I}Cu^{II}(μ_3-OH)](BAr$^F{}_4$)$_3$ (4b-BAr$^F{}_4$)



To an acetone (1 mL) solution of tetra-n-butylammonium chloride (60.8 mg, 0.219 mmol), an acetone (4 mL) solution of [**TREN$_4$**Cu^{I}Cu^{I}Cu^{II}(μ_3-OH)](PF_6)$_3$ (40.0 mg, 0.0292 mmol) was added dropwise with stirring. A blue precipitate was formed immediately and collected by filtration. After being washed by acetone (ca. 2 mL), the blue solid was dried under vacuum. Then, a dichloromethane (3 mL) suspension of the obtained blue solid was added to a dichloromethane (2 mL) suspension of sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate (103.5 mg, 0.117 mmol). The mixture was allowed to stir at room temperature overnight. After filtration, the blue filtrate was collected and dried under vacuum. The obtained blue solid was washed with diethyl ether (*ca.* 3 mL, three times) and dried under vacuum to afford the desired product **4b**-BAr$^F{}_4$ (98.3 mg, 96% yield).
Elemental analysis, Calcd for $C_{132}H_{109}B_3Cu_3F_{72}N_{16}O$ C, 44.96; H, 3.12; N, 6.36. found C,

44.65; H, 3.19; N, 6.23.

Synthesis and characterization of [TREN$_4$Cu^{I}Cu^{I}Cu^I(μ_3-OH)](PF$_6$)$_2$ (4a)

$$[\mathbf{TREN_4}Cu^{II}Cu^{I}Cu^{I}(\mu_3\text{-}OH)](PF_6)_3 + Cp_2Co \xrightarrow[\text{room temperature}]{\text{acetone, } N_2} [\mathbf{TREN_4}Cu^{I}Cu^{I}Cu^{I}(\mu_3\text{-}OH)](PF_6)_2$$

Yield: 19%

To an acetone (6 mL) solution of [**TREN$_4$**Cu^{I}Cu^{I}Cu^{II}(μ_3-OH)](PF$_6$)$_3$ (**4b**, 40.0 mg, 0.0292 mmol), an acetone (2 mL) solution of CoCp$_2$ (6.1 mg, and 0.0321 mmol, 1.1 eq) was added under nitrogen atmosphere. The mixture was stirred at room temperature for five minutes, during which the color of the solution turns yellow. All volatiles were removed under vacuum, and the yielded yellow residue was washed by THF (*ca.*15 mL). After dried under vacuum, the solid was dissolved in acetone (*ca.* 1.5 ml). Slow diffusion of diethyl ether to the acetone solution at –30 °C afford colorless crystals of **4a** (6.7 mg, yield 19%) suitable for XRD (Fig. S11). ^{1}H NMR analysis of the crystals (Fig. S3) shows a mixture of **4a** (marked with blue dots) and a small amount of impurity that appears to be the protonated species [**4a**+H] with sharp resonances at 9.20, 4.34, 3.30, 2.72, 2.45, and 2.36 ppm (marked with red dots, Fig. S3). We believe that the protonation of **4a** was due to the residual water in acetone-d_6, which cannot be completely removed without causing the decomposition of acetone-d_6. Unfortunately, we were unable to obtain a solution of **4a** in THF-d_8 due to its low solubility. Other NMR solvents, e.g. acetonitrile-d_3, cause rapid decomposition of **4a** back to **4b**. To confirm these sharp resonances (9.20, 4.34, 3.30, 2.72, 2.45, and 2.36 ppm) are from protonated **4a**, we prepared the BAr$^F_4$ analog **4a**-BAr$^F_4$, which can be dissolved and analyzed in THF-d_8 (*infra vide*).
Infrared spectrum, νOH = 3516 cm^{-1} (Fig. 6).

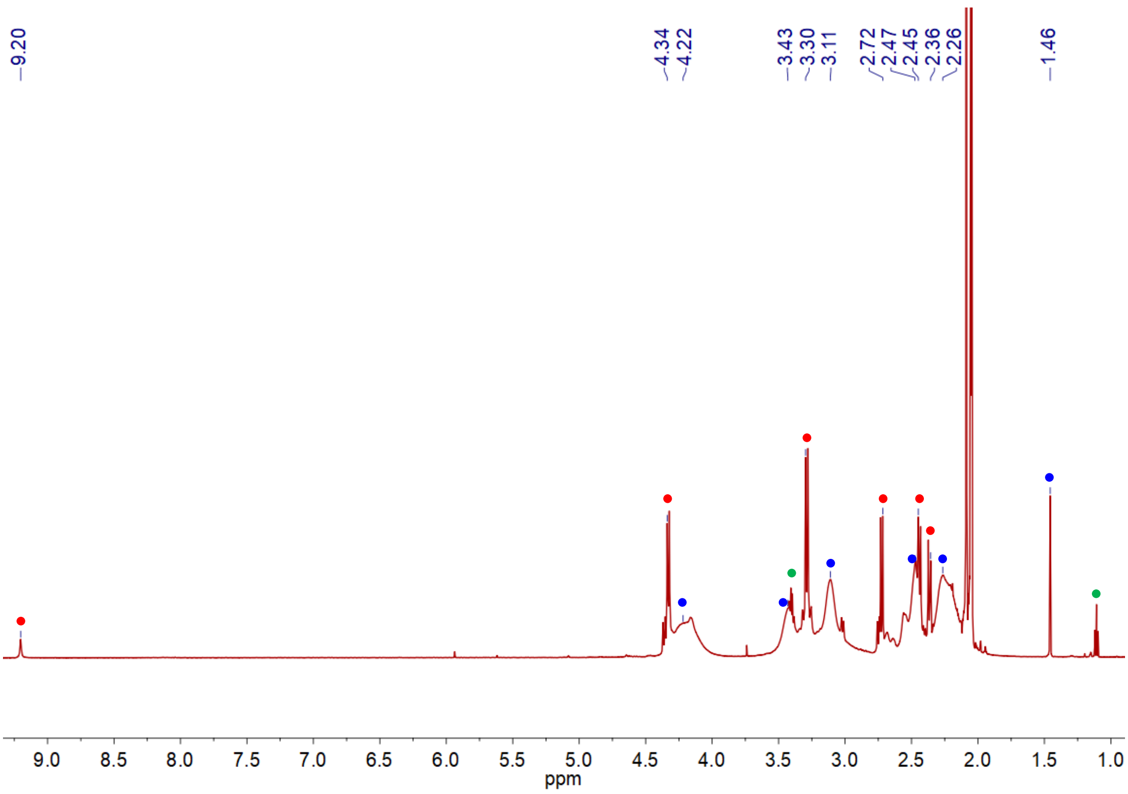


Fig. S3. ^{1}H NMR spectrum (600 MHz, acetone-d_6) of **4a** (blue dots). The peaks marked with green dots are from residual diethyl ether. The peaks marked with red dots are from protonated **4a**.

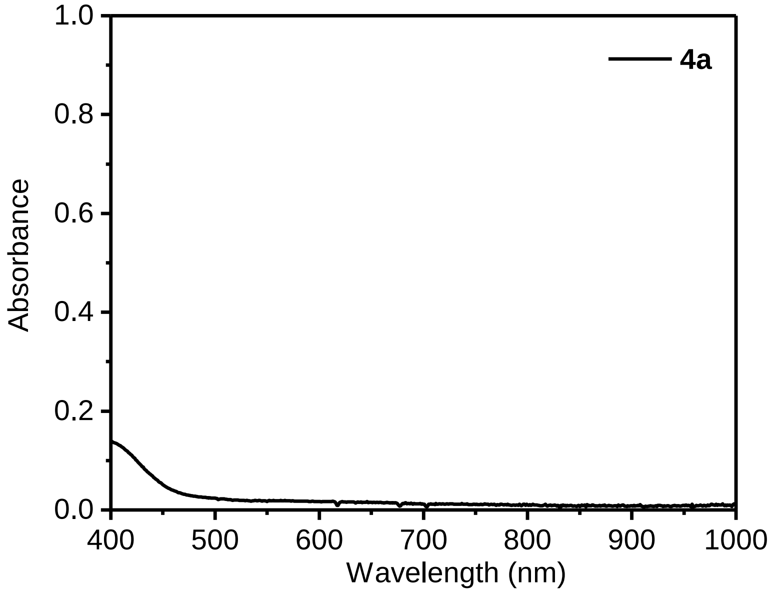


Fig. S4. UV-Vis spectrum of [**TREN$_4$**Cu^{I}Cu^{I}Cu^I(μ_3-OH)](PF$_6$)$_2$ (**4a**) in acetone at room temperature. The UV-Vis sample was generated in-situ from the treatment of [**TREN$_4$**Cu^{I}Cu^{I}Cu^{II}(μ_3-OH)](PF$_6$)$_3$ (**4b**) with one equivalent of Cp$_2$Co.

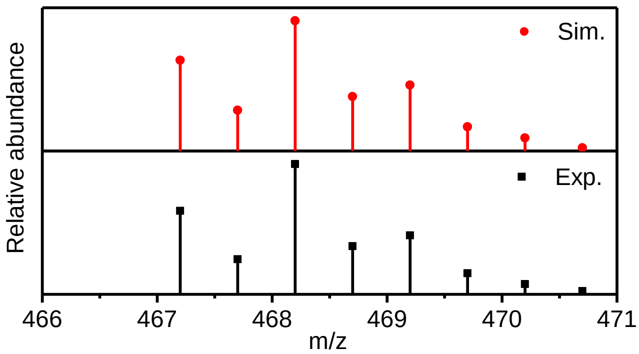
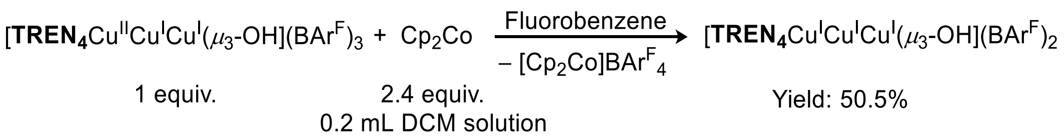


Fig. S5. ESI-MS spectrum (MeCN) and simulation of [**TREN$_4$**Cu^{I}Cu^{I}Cu^I(μ_3-OH)](PF$_6$)$_2$ (**4a**).

Synthesis and characterization of [TREN$_4$Cu^{I}Cu^{I}Cu^I(μ_3-OH)](BAr^F$_4$)$_2$ (4a-BAr^F$_4$)



To a suspension of **4b**-BAr^F$_4$ (10.0 mg, 0.00284 mmol) in fluorobenzene (1 mL), a dichloromethane (0.2 mL) solution of Cp$_2$Co (1.3 mg, 0.0068 mmol) was added with stirring. The blue **4b**-BAr^F$_4$ was gradually dissolved and the solution turned yellow. After filtration, the yellow filtrate was allowed to sit at room temperature overnight. Colorless needle-like crystals of **4a**-BAr^F$_4$ suitable for single-crystal X-ray diffraction were obtained. The mother liquid was pipetted out and the crystals were washed by fluorobenzene (*ca.* 5 mL) for three times. The obtained white solid was dissolved in THF (1.5 mL) and treated with triazabicyclodecene (2.0 mg, 0.014 mmol). After about one minute, the resulting suspension was filtered, and the filtrate was dried under vacuum. The obtained solid was washed with fluorobenzene (*ca.* 8 mL, five times) and dried under vacuum to afford **4a**-BAr^F$_4$ (3.8 mg, 51 % yield). (Fig. S12). ^{1}H NMR (600 MHz, THF-d_8, Fig. S6) δ 7.79 (br, 16H), 7.58 (br, 8H), 3.98 (br, 12H), 3.28 (br,

12H), 2.92 (br, 12H), 2.44 (br, 12H), 2.19 (br, 24H), 1.35 (s, 1H);
Elemental analysis, Calcd for $C_{100}H_{97}B_2Cu_3F_{48}N_{16}O$ C, 45.10; H, 3.67; N, 8.42. found C, 45.17; H, 3.84; N, 8.45.

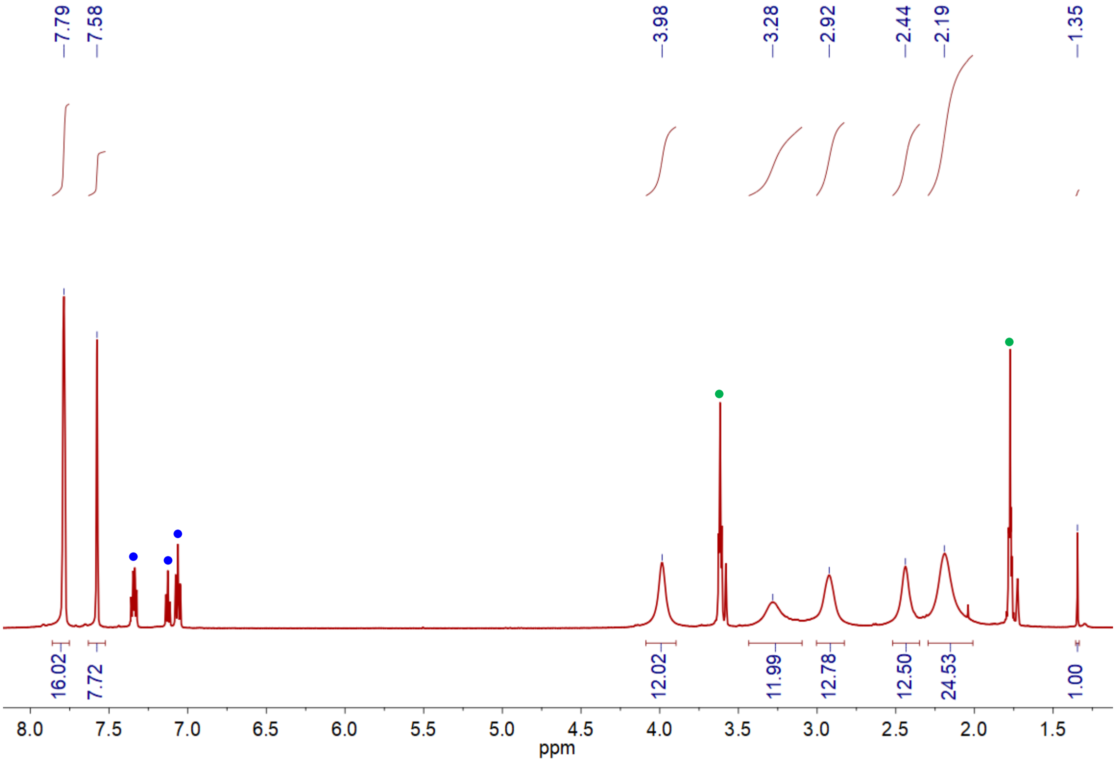
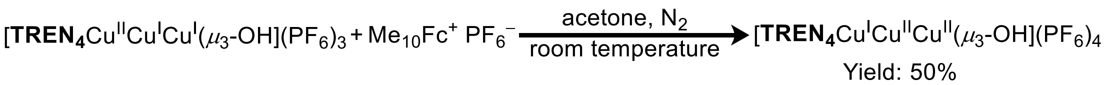


Fig. S6. ^{1}H NMR spectrum (600 MHz, THF-d_8) of **4a**-BAr$^F_4$. The peaks marked with blue dots are from residual fluorobenzene. The peaks marked with green spots are from residual THF.

Synthesis and characterization of [TREN$_4$Cu^{I}Cu^{II}Cu^{II}(μ_3-OH)] (PF$_6$)$_4$ (4c)



To an acetone (3 mL) solution of [**TREN$_4$**Cu^{I}Cu^{I}Cu^{II}(μ_3-OH)](PF$_6$)$_3$ (20.0 mg, 0.0140 mmol), an acetone (4 mL) solution of decamethylferrocenium hexafluorophosphate (9.4 mg, 0.020 mmol) was added under nitrogen atmosphere. The mixture was allowed to stir at room temperature for ten minutes. The solution was dried under vacuum and the yielded solid was re-dissolved in acetone (*ca.* 1 mL). THF (*ca.* 15 mL) was then added to the acetone solution with stirring. The obtained suspension was filtered and the dark blue precipitate was collected and dried under vacuum to afford **4c** (10.6 mg, 50 % yield) as a dark blue powder.
Elemental analysis, Calcd for **4c**•(CH$_3$C(O)CH$_3$)$_2$, $C_{42}H_{85}Cu_3F_{24}N_{16}OP_4$: C, 30.90; H, 5.25; N, 13.73. found C, 30.05; H, 5.26; N, 13.70.
UV-Vis spectrum (acetone, Fig. S7), λ_{max} = 680 nm (970 M^{-1}cm^{-1}), 850 nm (1250 M^{-1}cm^{-1});
Infrared spectrum, νOH = 3372 cm^{-1} (Fig. 6).

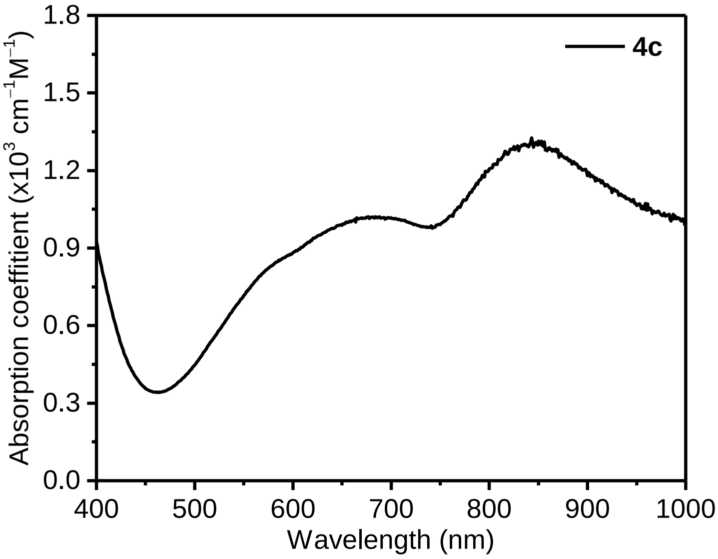


Fig. S7. UV-Vis spectrum of [**TREN$_4$**Cu^{I}Cu^{II}Cu^{II}(μ_3-OH)](PF_6)$_4$ in acetonitrile at room temperature. Two maxima at 680 nm and 850 nm were observed.

In order to obtain crystals of [**TREN$_4$**Cu^{I}Cu^{II}Cu^{II}(μ_3-OH)]$^{4+}$ for single-crystal X-ray diffraction analysis, [**TREN$_4$**Cu^{I}Cu^{II}Cu^{II}(μ_3-OH)](PF_6)$_4$ (10.0 mg, 0.00659 mmol) and tetra-n-butylammonium tetrafluoroborate ($TBABF_4$, 2.0 mg, 0.0060 mmol) was dissolved in acetone (*ca.* 1 mL). Slow diffusion of diethyl ether to the mixture of [**TREN$_4$**Cu^{I}Cu^{II}Cu^{II}(μ_3-OH)](PF_6)$_4$ and $TBABF_4$ at – 30°C afford single crystals of [**TREN$_4$**Cu^{I}Cu^{II}Cu^{II}(μ_3-OH)](PF_6)(BF_4)$_3$ (Fig. S13).

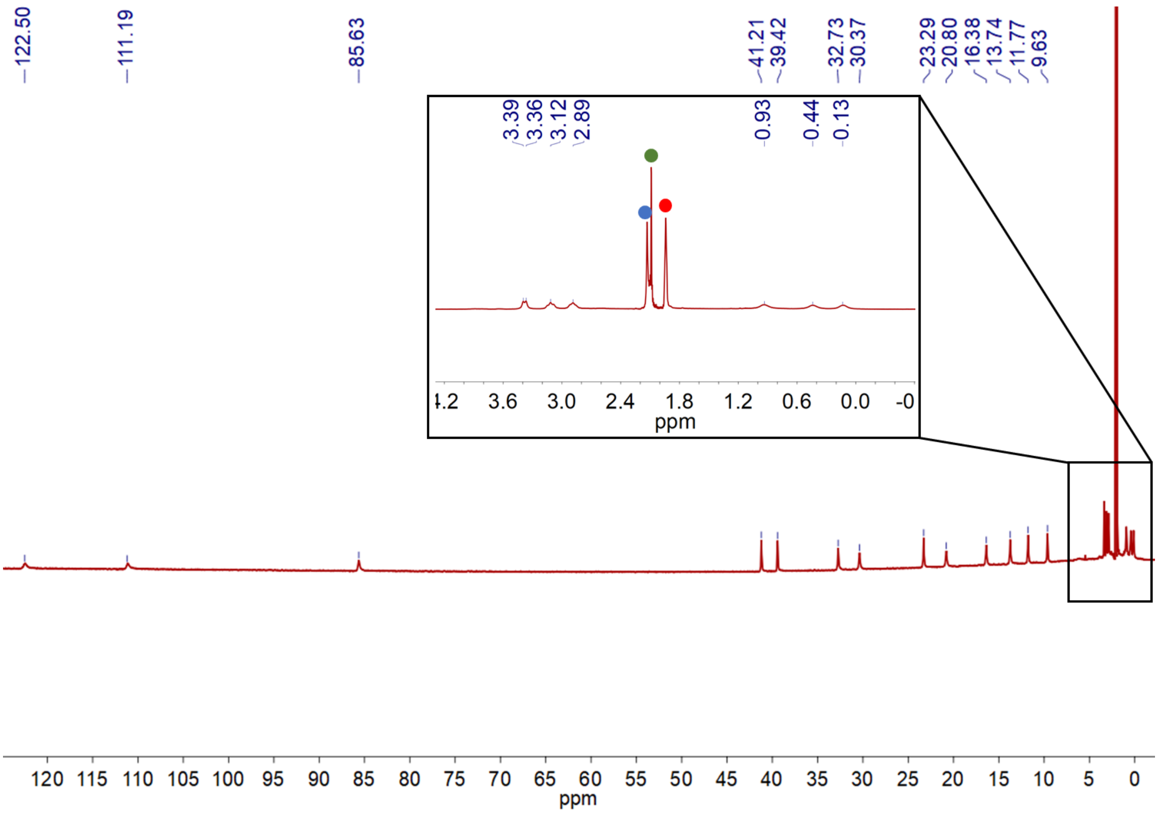


Fig. S8. ^{1}H NMR (400 MHz, CD_3CN) spectrum of [**TREN$_4$**Cu^{I}Cu^{II}Cu^{II}(μ_3-OH)](PF_6)$_4$ (**4c**).

The peak marked with a red dot is from residual CD_2HCN from the NMR solvent. The peak marked with a green dot is from residual acetone. The peak marked with a green dot is from residual water.

Synthesis and characterization of decamethylferrocenium hexafluorophosphate

$$\mathrm{Me_{10}Fc} + \mathrm{AgPF_6} \xrightarrow[\text{room temperature}]{\text{acetone, } N_2} \mathrm{Me_{10}Fc^{+}\,PF_6^{-}} + \mathrm{Ag}$$

Yield: 80%

To an acetone suspension (5 mL) of decamethylferrocene (154.6 mg, 0.4738 mmol), an acetone solution (2 mL) of $AgPF_6$ (100.0 mg, 0.3955 mmol) was added dropwise with stirring. The obtained mixture was allowed to stir at room temperature for three hours. After filtration, the green filtrate was collected and dried under vacuum. The green-yellow solid was then dissolved in acetone (*ca.* 5 mL). Diethyl ether (*ca.* 15 mL) was added to the acetone solution to precipitate out the product. The green solid was collected with filtration and dried under vacuum. Block crystals of the product were obtained by diffusing diethyl ether into an acetone solution (5 mL) at room temperature overnight (149.9 mg, Yield 80.3%).
Elemental analysis, Calcd for $C_{20}H_{30}F_6FeP$ C, 50.97; H, 6.42 found C, 51.42; H, 6.38.

2. UV-Vis spectroscopy Studies Details

Determining the molar extinction coefficient of NaI_3 in an acetone/heptane (2:3) mixture

$$NaI + I_2 \longrightarrow NaI_3$$

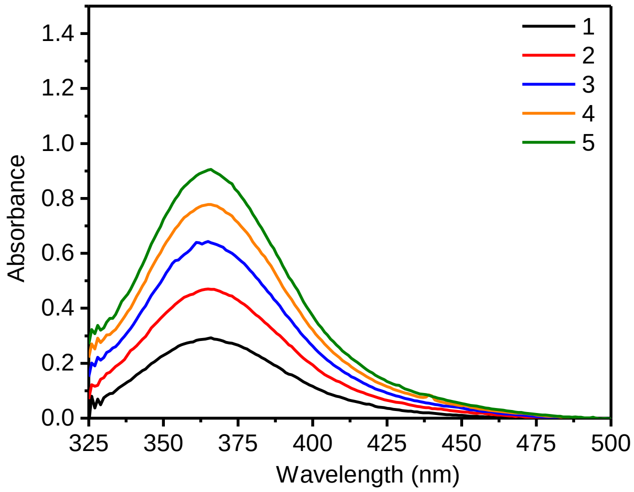
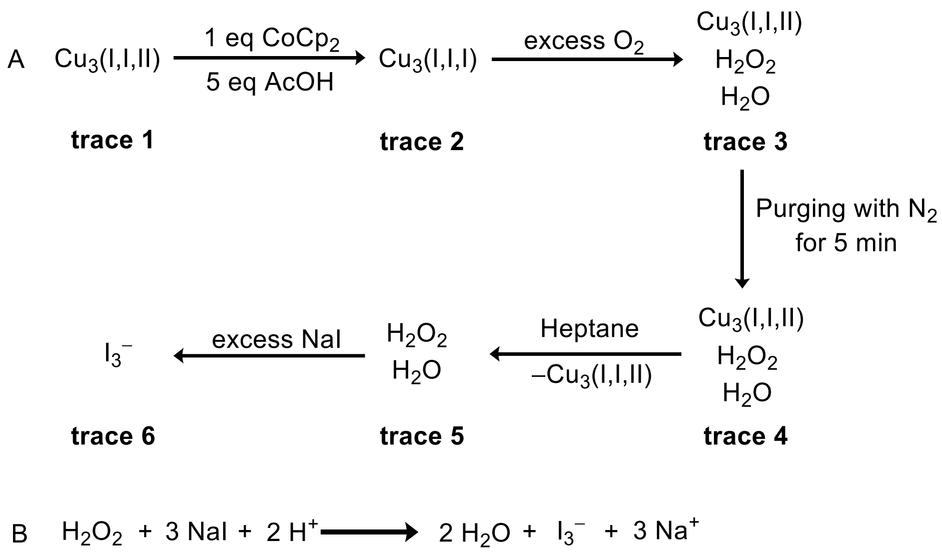


Fig. S9. Solutions of NaI_3 with various concentrations were prepared by adding a solution of I_2 (0.2 mL, 1.2 mM) to NaI (2 mL, 50 mM, excess) in acetone/heptane (2:3) sequentially. The UV-Vis traces of the solutions were recorded at 0.0109 mM (trace 1), 0.0200 mM (trace 2), 0.0277 mM (trace 3), 0.0343 mM (trace 4), and 0.0400 mM (trace 5). The molar extinction coefficient of NaI_3 at 364 nm was calculated as 2.13×10^4 $cm^{-1}M^{-1}$.

Quantification of H_2O_2 produced from the reaction of 4a and O_2



Scheme S1. (A) H_2O_2 quantification from the stoichiometric reaction between **4a** and O_2. (B) The reaction of H_2O_2 and NaI.

In glovebox, an acetone solution of [**TREN₄**$Cu^{I}Cu^{I}Cu^{II}$(μ_3-OH)](PF_6)$_3$ (**4b**, 1.4 mg, 1.0 μmol, 2.00 mL, 0.5 mM) was transferred to a Schlenk quartz cuvette. The cuvette was sealed and transferred to the UV-Vis spectrometer (Fig. S9, trace 1). Under nitrogen protection, an acetone solution of Cp_2Co (0.19 mg, 1.0 µmol, 0.500 mL acetone) and acetic acid (0.30 mg, 5.0 µmol, 5 equiv., 0.500 mL acetone) were injected to the cuvette. The 790 nm and 655 nm bands of complex **4b** ($Cu^{II}Cu^{I}Cu^{I}$) were bleached instantaneously (Fig. S10, trace 2, Scheme 1), indicating the formation of complex **4a** ($Cu^{I}Cu^{I}Cu^{I}$). Oxygen gas (0.500 ml, 20.5 µmol, 20.5 equiv.) was injected to the cuvette (Fig. S10, trace 3). The progress of oxygen reduction reaction was monitored by taking a UV-Vis spectrum every 60 seconds. Two bands at 790 nm and 655 nm grew in over 5 minutes, indicating the reformation of complex **4b** ($Cu^{II}Cu^{I}Cu^{I}$) in 96% spectroscopic yield. The solution in the Schlenk quartz cuvette was purged with N_2 for five minutes to remove the excess oxygen (Fig. S10, trace 4). The cuvette was sealed and transferred back into glovebox. The solution in cuvette was transferred to a scintillation vial. The cuvette was washed with additional acetone (1 mL) to ensure complete transfer. Additional acetone (0.354 mL, calculated based on absorbance increase at 790 nm after purging) was added to the scintillation vial in order to compensate the solvent loss during the N_2 purging process. To the combined acetone solution, heptane (6 ml) was added in order to precipitate out all the copper complexes. The obtained suspension was then filtered, and the filtrate (2 mL) was transferred to a new Schlenk quartz cuvette (Fig. S10, trace 5). Acetone/heptane (2:3) solution of NaI (7.5 mg, 50 µmol, 0.500 mL) was injected to the solution in the cuvette (Fig. S10, trace 6). The reaction between H_2O_2 and NaI affords I_3^- (Scheme S1, B), the yield of which can be determined by its characteristic absorbance at λ_{max} = 364 nm ($\varepsilon = 2.1 \times 10^4$ M^{-1} cm^{-1}). The H_2O_2 quantification results from three independent trials are summarized in Table S1.

Entry	Experiment 1	Experiment 2	Experiment 3	average
Absorbance / I_3^-	0.817	0.813	0.847	0.826
Amount / mmol	9.57×10^{-5}	9.52×10^{-5}	9.92×10^{-5}	9.67×10^{-5}
Yield of H_2O_2	96%	95%	99%	97%

Table S1. Yields of H_2O_2 in three independent trials.

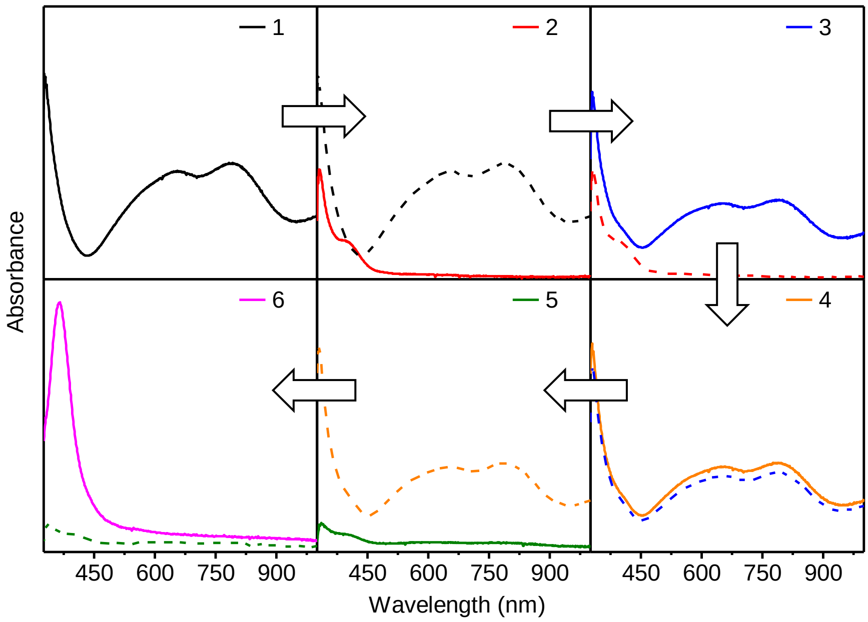


Fig. S10. UV-Vis traces for H_2O_2 quantification. The absorbances of the spectra were normalized based on solution volume to account for dilution.

3. X-ray Crystallographic Data

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon II CPAD diffractometer equipped with Cu K_α radiation (λ = 1.54178) for **4a**, a Bruker Kappa Photon II CPAD diffractometer equipped with Mo K_α radiation (λ = 0.71073 Å) for **4b**, and a Nonius Kappa diffractometer equipped with a Bruker APEX-II CCD and Mo K_α radiation (λ = 0.71073 Å) for **4c**. Crystals were mounted on MiTeGen Micromounts with Paratone oil, and data were collected in a nitrogen gas stream at 100 K. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model for refinement. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Due to the disorder of the Cu positions in the structure, the hydroxide hydrogen atoms were placed at idealized locations and restrained using DFIX commands to fit to the disorder model of each structure. Their thermals were fixed to that of the parent oxygen atom. Platon SQUEEZE was used to remove the electron density from the lattice due to the disordered solvent contribution. **4a** and **4b** both had 4 voids with 34 electrons in each. **4c** had 2 large voids of 600 electrons. In all cases, the disordered solvent appeared to be a mixture of acetone and diethyl ether.

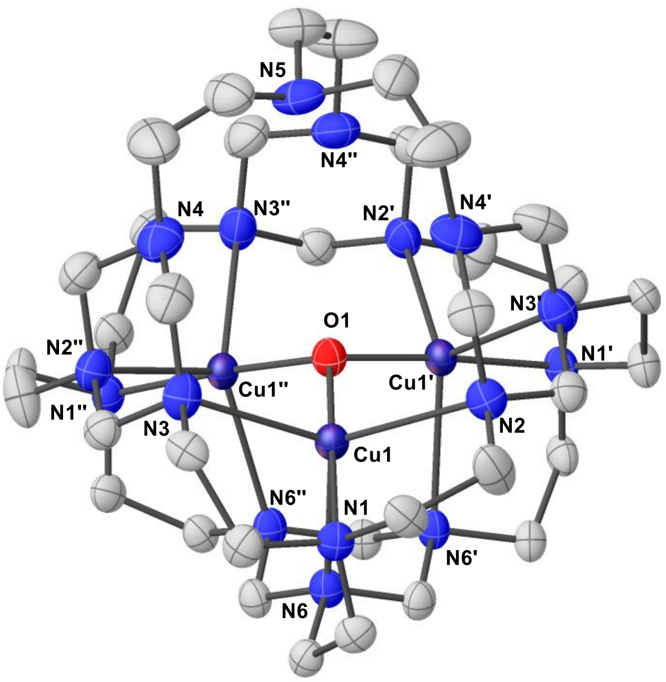


Fig. S11: X-ray structure (CIF: 1984893, 100 K) of **4a** with thermal ellipsoids of 20% probability. Hydrogen atoms and anion PF_6^- are omitted for clarity. Selected bond lengths (Å) for **4a**: Ave. Cu–O = 1.885(5), Ave. Cu…Cu = 3.098, Cu–N = 2.057-2.538.

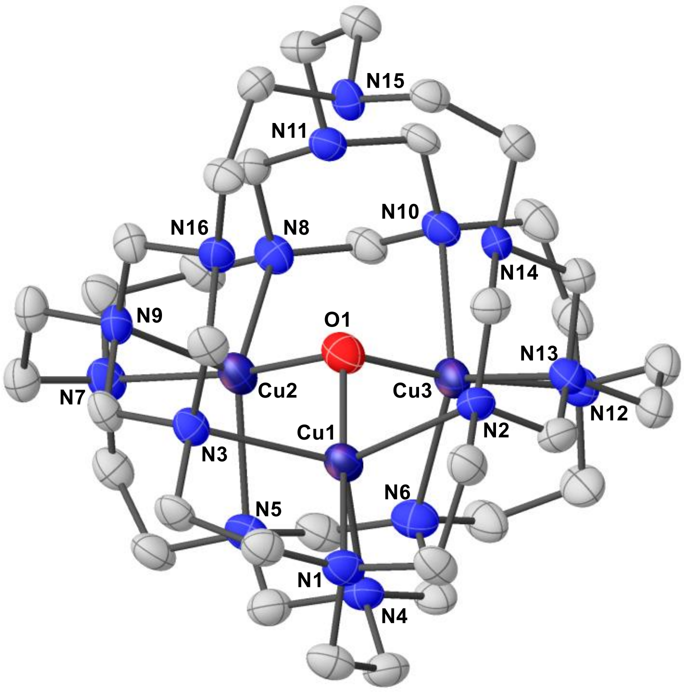


Fig. S12: X-ray structure (CIF: 1984894, 100 K) of **4b** with thermal ellipsoids of 50% probability. Hydrogen atoms, solvent molecules, and anion PF_6^- are omitted for clarity. Selected bond lengths (Å) for **4b**: Ave. Cu–O = 1.913(6), Ave. Cu⋯Cu = 3.112, Cu–N = 2.060-2.491.

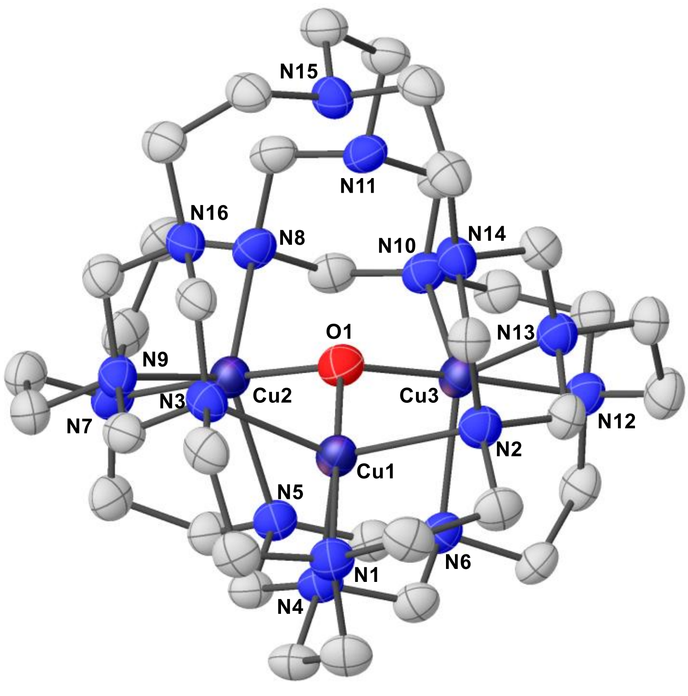


Fig. S13: X-ray structure (CIF: 1984895, 100 K) of **4c** with thermal ellipsoids of 30% probability. Hydrogen atoms, solvent molecules, and anion BF_4^-/PF_6^- are omitted for clarity. Selected bond lengths (Å) for **4c**: Ave. Cu–O = 1.937(3), Ave. Cu⋯Cu = 3.181, Cu–N = 2.093-2.300.

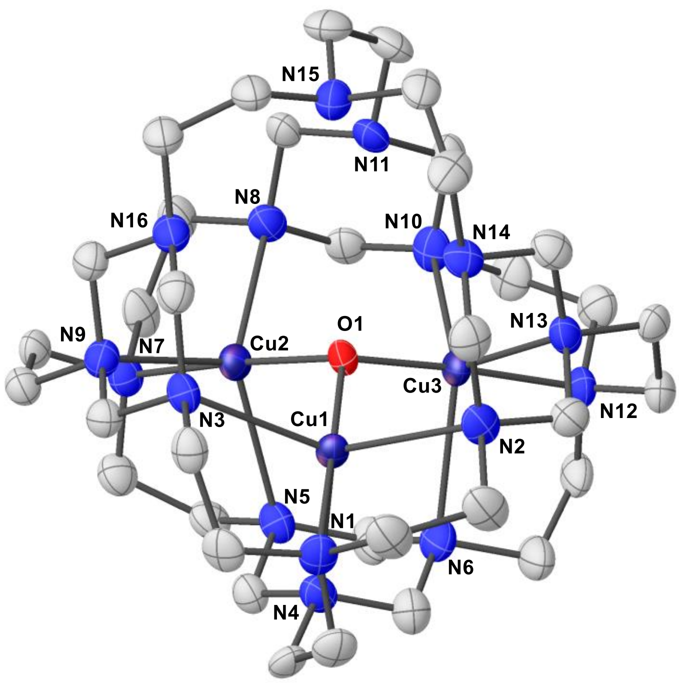


Fig. S14: X-ray structure (CIF: 1987932, 100 K) of **4a**-BAr^F_4 with thermal ellipsoids of 50% probability. Hydrogen atoms, solvent molecules, and anion $BAr^F_4{}^-$ are omitted for clarity. Selected bond lengths (Å) for **4a**-BAr^F_4: Ave. Cu–O = 1.913(2), Ave. Cu···Cu = 3.129, Cu–N = 2.049-2.559.

Table S2: Crystal Data and Structure Refinement for **4a**, **4b**, **4c**, and **4a**-BAr^F_4.

	4a	**4b**	**4c**	**4a**-BAr^F_4
CCDC	1984893	1984894	1984895	1987932
Empirical formula, FW (g/mol)	$C_{36}H_{73}Cu_3F_{12}N_{16}OP_2$, 1226.64	$C_{45}H_{91}Cu_3F_{18}N_{16}O_4P_3$, 1545.70	$C_{39}H_{79}B_3Cu_3F_{18}N_{16}O_2P$, 1400.20	$C_{100}H_{97}B_2Cu_3F_{48}N_{16}O$, 2663.17
Color	Colorless Block	Blue Block	Blue Block	Colorless Block
Temperature (K)	100	100	100	100
Wavelength (Å)	1.54178	0.71073	0.71073	0.71073
Crystal system, Space group	Cubic, Pa-3	Monoclinic, C 1 c 1	Monoclinic, C 1 2/c 1	Triclinic, P-1
Unit cell dimensions a (Å)	17.4900(2)	22.6031(11)	35.673(3)	12.4878(13)
b (Å)	17.4900(2)	17.2489(8)	21.1666(16)	15.1031(17)
c (Å)	17.4900(2)	17.6361(8)	21.0194(17)	15.1131(17)
α(°)	90°	90	90	77.567(3)
β(°)	90°	100.981(2)	102.442(2)	88.651(3)
γ(°)	90°	90	90	85.637(3)
Volume (Å^3)	5350.19(18)	6750.0(5)	15498(2)	2775.4(5)
Z	4.00008	4	8	1
Density (calc., g/cm^{-3})	1.523	1.521	1.200	1.593
Absorption coefficient (mm^{-1})	2.729	1.108	0.917	0.706
F(000)	2536	3196	5760	1346
Theta range for data collection (°)	6.198 to 68.078	2.932 to 25.393	1.126 to 25.437	3.113 to 25.380

Index ranges	-20<=h<=19, -20<=k<=20, -16<=l<=20	-27<=h<=27, -20<=k<=20, -20<=l<=21	-42<=h<=43, -25<=k<=25, -25<=l<=24	-15<=h<=15, -18<=k<=18, -18<=l<=18
Reflections collected	33351	82474	205973	111075
Independent reflections, R_{int}	1628 [R(int) = 0.0331, R(sigma) = 0.0104]	12117 [R(int) = 0.0465, R(sigma) = 0.0347]	14249 [R(int) = 0.0763, R(sigma) = 0.0452]	10153 [R(int) = 0.0801, R(sigma) = 0.0439]
Completeness to $2\theta_{max}$ (%)	99.4	99.2	99.9	99.8
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1628 / 196 / 201	12117 / 194 / 867	14249 / 52 / 837	10153 / 564 / 1124
Goodness-of-fit	1.047	1.037	1.028	1.128
Final R indices [I>2sigma(I)]	R1 = 0.0679, wR2 = 0.1844	R1 = 0.0530, wR2 = 0.1221	R1 = 0.0616, wR2 = 0.1770	R1 = 0.0791, wR2 = 0.1663
Largest diff. peak and hole ($e \cdot$ Å^{-3})	0.359 and -0.218	0.479 and -0.470	0.732 and -0.316	0.409 and -0.546

4. ESI-MS details

ESI-MS analysis of the reaction of complex 4a and $^{18}O_2$ in the presence of acetic acid

To an acetone solution (5 mL) of complex **4b** (2.2 mg, 0.0016 mmol) in a 20 mL scintillation vial equipped with a septum, $CoCp_2$ (0.27 mg, 0.0015 mmol) was added under nitrogen atmosphere to generate complex **4a** in situ. Excess $^{18}O_2$ (0.5 mL, 0.02 mmol) and acetic acid (2.1 mg, 0.035 mmol) was inject to the vial and the obtained mixture was allowed to stir at room temperature for five minutes, during which the color of the solution changed from yellow to blue, indicating complex **4a** was oxidized back to complex **4b**. ESI-MS analysis of the resulting blue solution (Fig. S15) showed that less than 10% of μ_3-^{16}O ligand in **4a** was replaced by ^{18}O during its aerobic oxidation to **4b**.

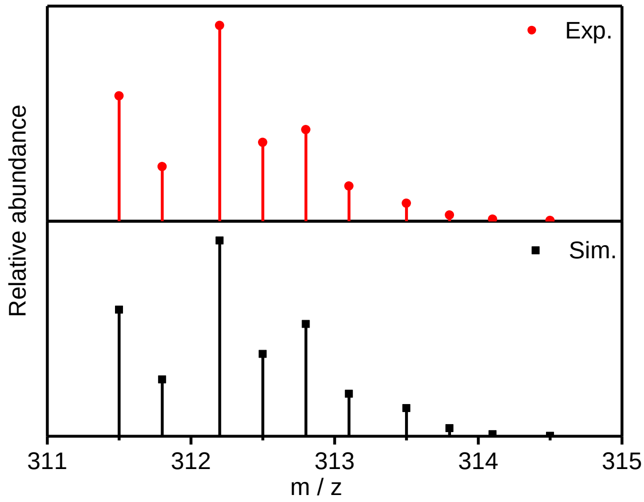


Fig. S15. ESI-MS analysis of complex **4b** from the reaction of complex **4a** and $^{18}O_2$ in the presence of acetic acid (red), and simulated mass spectrum with 90% **4b-**^{16}O and 10% **4b-**^{18}O (black).

5. X-band EPR details

EPR spectra were recorded on a Bruker EMXPlus X-band EPR spectrometer equipped with Coldedge cryostat with small-volume power saturation. All samples were measured in 4 mm septum-capped EPR quartz tubes (Wilmad Lab glass, 727-SQ-250MM). Complex **4b** (4.1 mg, 3 μmol) was dissolved in acetonitrile (6.0 mL) to make a 0.50 mM solution of **4b**, and 0.20 mL of the solution was transferred into the EPR tube under nitrogen atmosphere, frozen in liquid nitrogen, and used for EPR measurement. The spectrum was collected at 50 K with a modulation frequency of 100 kHz and a modulation amplitude of 10 G using 30 dB attenuation. A time constant of 40.96 ms and a conversion time of 50.15 ms were used. All spectra were baseline-corrected using Igor Pro (Wavemetrics, Lake Oswego, OR) software. Spectral simulations were performed using the EasySpin toolbox with MATLAB.[2]

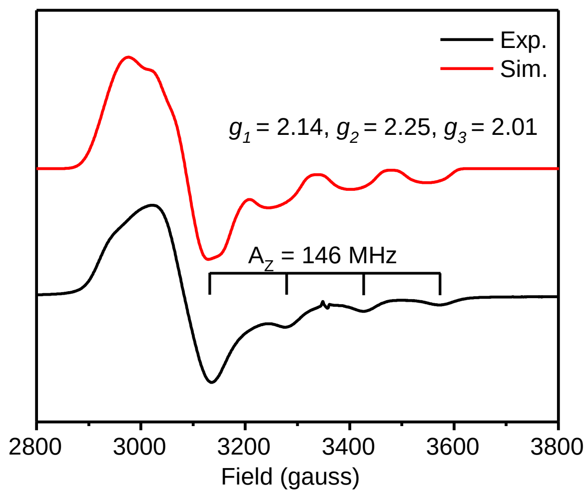


Fig. S16. X-band EPR spectrum (frozen MeCN, 50K, 0.5 mM) of complex **4b**; g_1 = 2.14, g_2 = 2.25, g_3 = 2.01, A_3 = 146 MHz.

6. Electrochemistry details

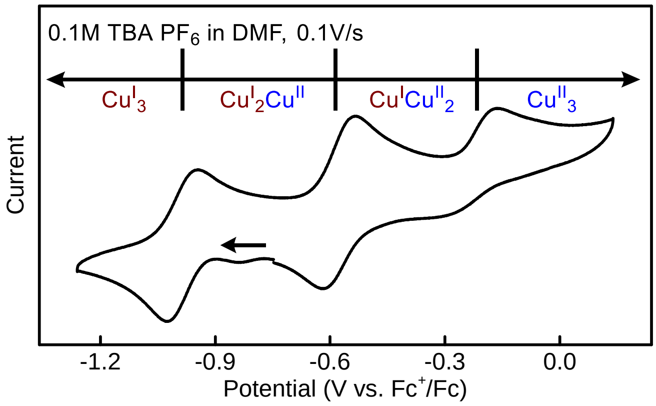


Fig. S17. Solution cyclic voltammogram of **4b** (1 mM) in DMF (0.1 M $TBAPF_6$) with a scan rate of 0.100 V/s. Working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: $Ag/AgNO_3$.

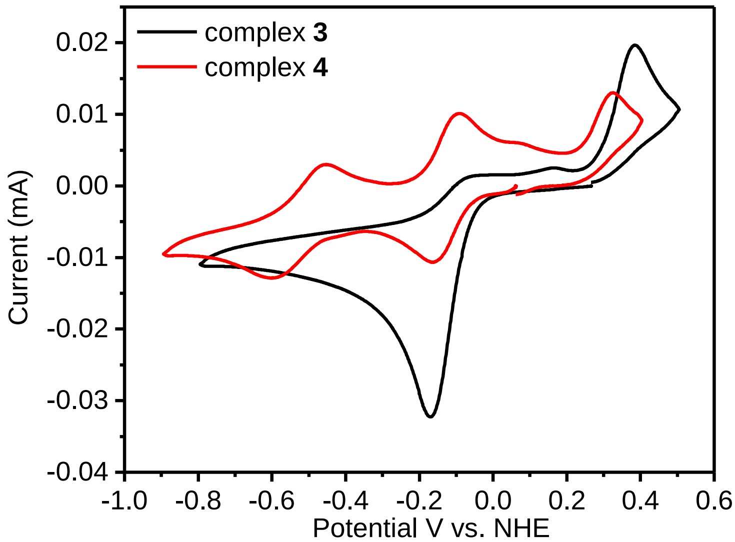


Fig. S18. Solution cyclic voltammogram of **4** (1 mM) and **3** (1 mM) in phosphate buffer (pH = 5.8, 0.1 M) with a scan rate of 0.100 V/s. Working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: leakless Ag/AgCl electrode (eDAQ).

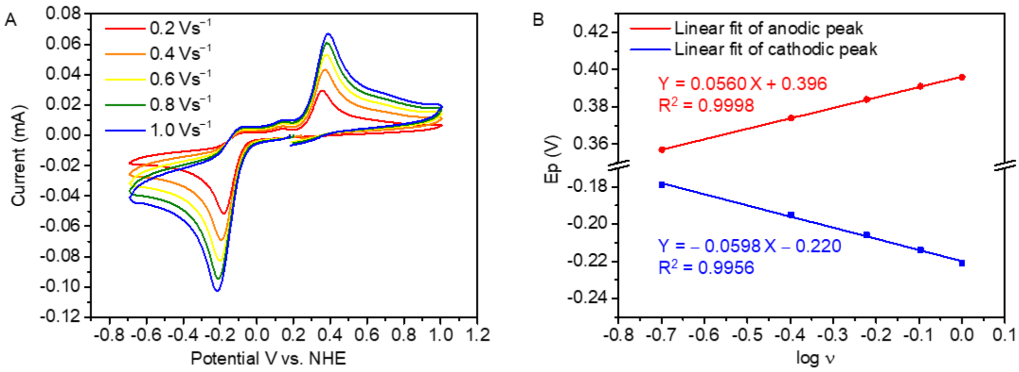
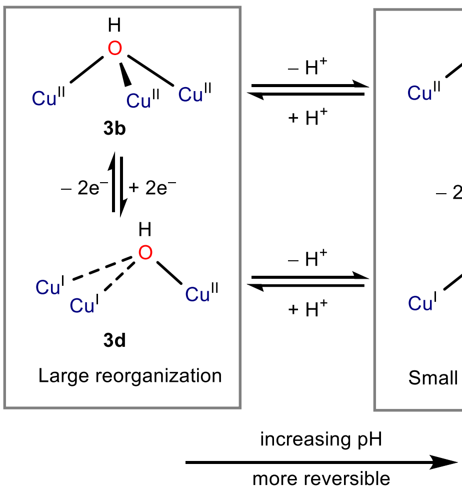


Fig. S19. (A) Scan rate dependant cyclic voltammetry of **3a** (1 mM, pH = 5.8 phosphate buffer). (B) Plot of cathodic and anodic potentials against log ν (scan rate, V/s). The number of electrons involved in the redox process can be calculated using Laviron's equation.[3] The slope obtained from the plot is equal to:

$$\frac{2.3RT}{\alpha Fn}$$

where α is the electron-transfer coefficient and assumed to be 0.5 for irreversible process.[4] R (8.314 $J \cdot K^{-1} \cdot mol^{-1}$) is the ideal gas constant. T (298K) is temperature. F (96485 $C \cdot mol^{-1}$) is Faraday constant. n is the number of electrons involved. n_c, the number of electrons involved in the cathodic process, was calculated to be 2.0. And n_a, the number of electrons involved in the anodic process, was calculated to be 2.1. This result suggests that both the oxidation and the reduction are two-electron processes.



Scheme S2. Proposed redox behavior of **3a** based on its CV at different pH. Under acidic conditions, **3a** is protonated to form **3b** with a μ_3-hydroxo ligand. The *ca.* 800 μV separation of the redox couple at low pH indicates a substantial barrier for electron transfer. Under basic conditions, **3b** is deprotonated to afford **3a**. The central μ_3-oxo ligand in **3a** binds to the three copper centers tighter than μ_3-hydroxo, attenuating the redox-induced geometric change and lowering the barrier for electron transfer. Consequently, the redox of **3a** is more reversible under basic conditions.

Evaluation of the electron self-exchange rate constants k_{el} and k_{hom}.

The standard electrochemical electron self-exchange rate constant k_{el} (cm s^{-1}) for the **4a**/**4b** and **4b**/**4c** redox couples was estimated using an electrochemical method published previously.[5] Under quasi-reversible conditions, k_{el} can be derived from Eq. 1:[6,7]

$$\Psi = k_{el}(D_R/D_O)^{\alpha/2}(RT/nF\pi D_R)^{1/2}\nu^{-1/2} \qquad (1)$$

where Ψ is a kinetic parameter, D_R and D_O are the diffusion coefficients (cm^2/s) of the reduced and oxidized species, respectively, α is the transfer coefficient for the electrode process, R is gas constant (8.314 J K^{-1} mol^{-1}), T is temperature (T = 298.15 K in this case), n is the number of electrons transferred in each step (n = 1 in this case), F is Faraday constant (96485.3 C mol^{-1}), and ν is the potential scan rate (V s^{-1}). The kinetic parameter Ψ is also related to the peak-to-peak separation (ΔE_p / mV) of the anodic and cathodic waves in cyclic voltammogram by using the empirical equation (Eq. 2):[6]

$$\Psi = (-0.6288+0.0021n\Delta E_p)/(1-0.017n\Delta E_p) \qquad (2)$$

where n is the number of electrons transferred in each step. Cyclic voltammograms of **4a**/**4b** and **4b**/**4c** (1 mM in MeCN + 0.1 M Bu_4NPF_6) were measured at different potential scan rates (0.5-5.0 V s^{-1} range) in the suitable potential regions (Fig. S20A and S20C). Current interrupt (CI) measurement was performed before the cyclic voltammetry to account for uncompensated resistance (R_u). The values of Ψ were calculated from the experimental ΔE_p values (80 mV – 140 mV) using the Eq. 2. The value of D_O and D_R was obtained using the Randles-Sevcik equations (9.4(6)×10^{-7} cm^2 s^{-1} and 9.4(6)×10^{-7} cm^2 s^{-1} for **4a**/**4b** redox couple; 1.5(1)×10^{-6} cm^2 s^{-1} and 1.4(1)×10^{-6} cm^2 s^{-1} for **4b**/**4c** redox couple). Since $D_O \approx D_R$ in both redox cases and $0< \alpha <1$, $(D_R/D_O)^{\alpha/2}$ is approximated equal to 1.[7] An estimate of the values of k_{el} was obtained from the Ψ vs $\nu^{-1/2}$ plot using Eq. 1 (7.8(2)×10^{-3} cm s^{-1} for **4a**/**4b** redox couple, Fig.S19B; 7.6(2)×10^{-3} cm s^{-1} for **4b**/**4c** redox couple, Fig.S19D). A correlation between k_{el} and the homogeneous electron self-exchange rate constant k_{hom} (L mol^{-1} s^{-1}) has been described by Weaver et al. (Eq. 3):[8]

$$k_{hom} = 4\pi N_A r_h^2 k_{el} 10^{-19} \qquad (3)$$

where k_{el} is the electrochemical rate constant (cm s^{-1}), N_A is the Avogadro constant (mol^{-1}), and r_h is the internuclear distance for self-exchange (Å). The value of r_h (11.2 Å) was estimated based on atomic coordinate of the X-ray single-crystal structure **4b** using chemcraft software. The value of k_{hom} was calculated as 7.4(2)×10^5 L mol^{-1} s^{-1} for 4**a**/4**b** redox couple and 7.2(2)×10^5 L mol^{-1} s^{-1} for 4**b**/4**c** redox couple.

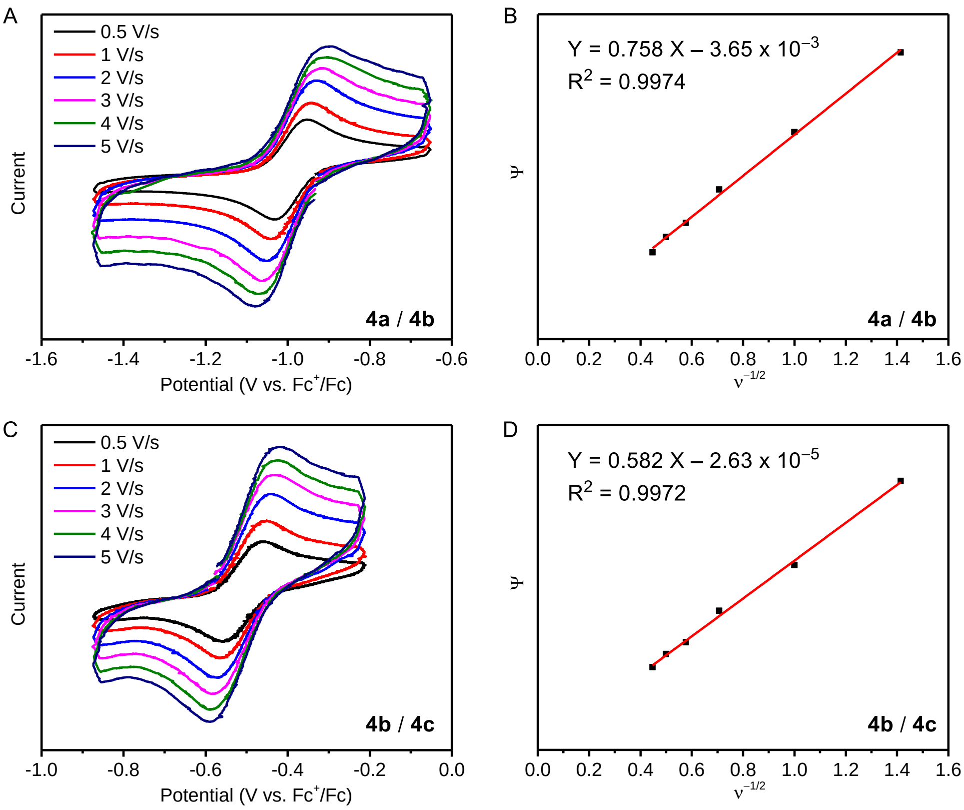


Fig. S20. Scan rate dependent cyclic voltammograms for **4a**/**4b** redox couple (A) and **4b**/**4c** redox couple (C).Ψ vs $\nu^{-1/2}$ plots for **4a**/**4b** redox couple (B) and **4b**/**4c** redox couple (D).

7. Computational details

All computations were performed using ORCA software packages.[9] The geometry optimization was carried out using BP86 method with a mixed basis set (def2-TZVP for the copper atoms and def2-SVP for all light atoms, C, N, O, H), followed by a frequency calculation. For both complex **3** and **4** in $Cu^{I}Cu^{II}Cu^{II}$ and $Cu^{II}Cu^{II}Cu^{II}$ oxidation states, the structures were optimized at three spin states (singlet, triplet, broken symmetry triplet for $Cu^{I}Cu^{II}Cu^{II}$; doublet, quartet, and broken symmetry quartet for $Cu^{II}Cu^{II}Cu^{II}$) at BP86/def2-TZVP(Cu)/def2-TZVP(C, N, O, H) level of theory to determine the ground state (Table S3). To estimate the reorganization energy (λ), single-point calculations of the one-electron oxidized or reduced species at their redox counterpart's geometry were performed. The implication of reorganization energy for the oxidized complex (λ_{ox}) and the reduced complex (λ_{red}) of a redox couple is clarified in Fig. S21. The total inner-sphere reorganization energy for a self-exchange reaction (λ_i) is the sum of λ_{ox} and λ_{red}. Solvated single-point energies were calculated at TPSSh/def2-TZVP(Cu)/def2-SVP(C, N, O, H) level[10] with a continuum solvation model (SMD, acetonitrile).[11] Dispersion corrections with Becke-Johnson damping were applied for single-point calculation.[12,13] The Gibbs free energy of each species was determined by adding the solvated single point SCF energy to the thermal correction from the respective frequency calculation.[14] The results are shown in Table S4. Time-dependent density-functional theory (TD-DFT) calculation for complex **4b** and **4c** were performed at TPSSh/def2-TZVP level using 50 roots.

Oxidation state	Spin state	[**TREN$_3$**Cu$_3$O]/Ha	[**TREN$_4$**Cu$_3$OH]/Ha
I II II	Singlet	–6598.60730064[a,b]	–
	Triplet	–6598.63490810[a,b]	Exp. Ground state
	Triplet Broken-symmetry	–6598.62889281[a,b]	–
II II II	Doublet	–6598.15449969[a,b]	–7284.95586835[a,b]
	Quartet	–6598.15523773[a,b]	–7284.96125714[a,b]
	Quartet Broken-symmetry	–6598.15451636[a,b]	–7284.95890205[a,b]

a: TPSSh/SVP; b: SCF single point energy

Table S3: Ground state determination of complex **3** and **4** at the $Cu^{I}Cu^{II}Cu^{II}$ and $Cu^{II}Cu^{II}Cu^{II}$ oxidation states. The isolated [**TREN$_4$**Cu$_3$OH] in $Cu^{I}Cu^{II}Cu^{II}$ oxidation has a paramagnetic ^{1}H NMR, which suggests its triplet ground state.

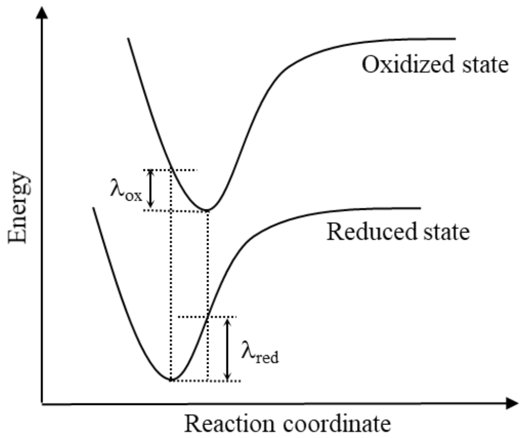
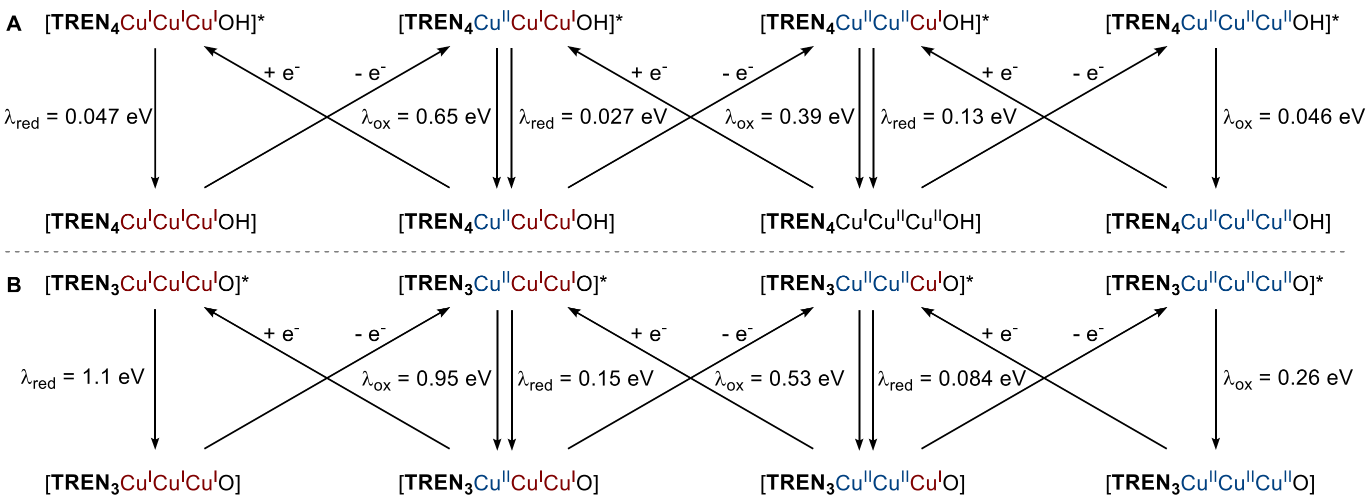


Fig. S21. The potential energy of a general electron transfer. The reorganization energy of the reduction and the oxidation (λ_{ox} and λ_{red}) are indicated.



Scheme S3. Computed inner-sphere reorganization energy of (A) **4** and (B) **3.** l_{ox} and l_{red} can be computationally estimated by the energy required to distort the equilibrium geometries to their redox-partners' geometries. For example, λ_{ox} of **4a**/**4b** couple is the energy of **4b** calculated at **4a**'s optimal geometry minus the energy of **4b** at its optimal geometry. Similarly, the l_{red} of **4a**/**4b** couple is the energy of **4a** calculated at **4b**'s optimal geometry minus the energy of **4a** at its optimal geometry.

Complex	Redox couple	λ_{ox}	λ_{red}	λ_i
Complex **4**	I,I,I – I,I,II	0.047	0.65	0.70
	I,I,II – I,II,II	0.027	0.39	0.42
	I,II,II – II,II,II	0.13	0.046	0.18
Complex **3**	I,I,I – I,I,II	1.1	0.95	2.1
	I,I,II – I,II,II	0.15	0.53	0.68
	I,II,II – II,II,II	0.084	0.26	0.34

Table S4. The calculated λ_{ox}, λ_{red}, and λ_i (eV) for complex **3** and **4**.

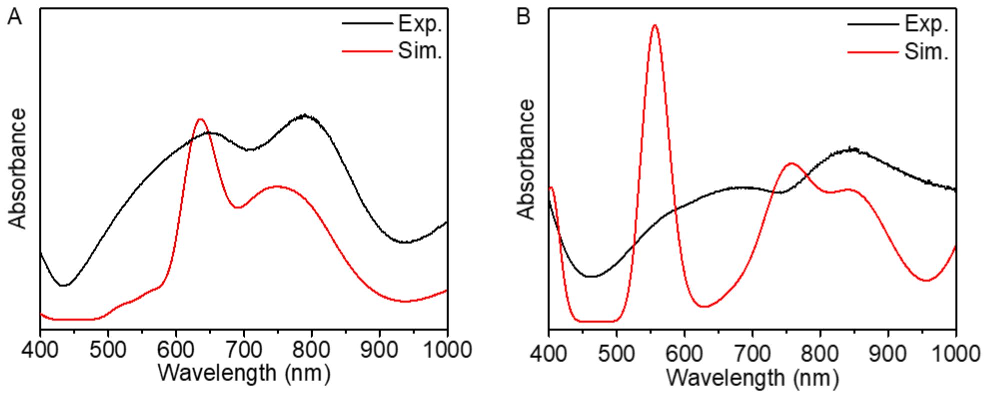


Fig. S22. Experimental and simulated UV-vis spectrum of complex **4b** (A) and **4c** (B).

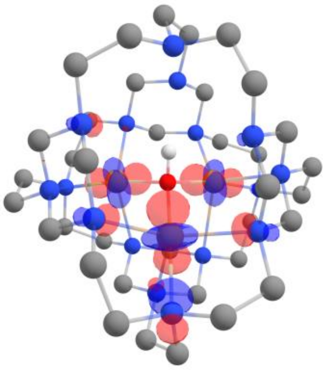
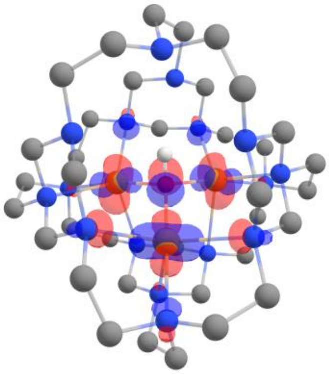
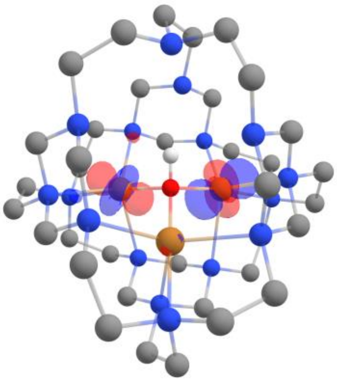
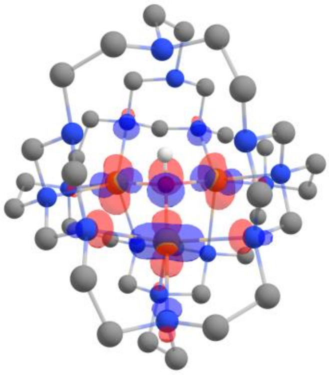
Transitions (nm)	Donor orbital	Acceptor orbital
634 nm		
775 nm		

Table S5: Selected TD-DFT transitions for **4b**. Orbitals plotted at a 0.048 isosurface value.

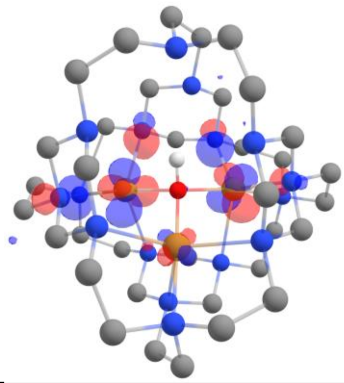
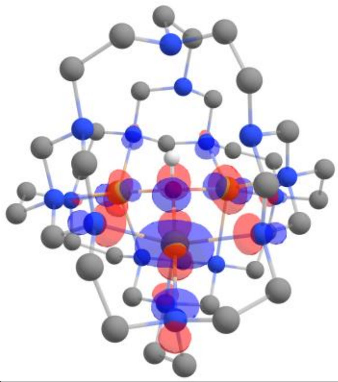
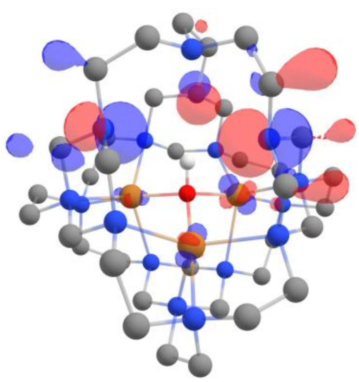
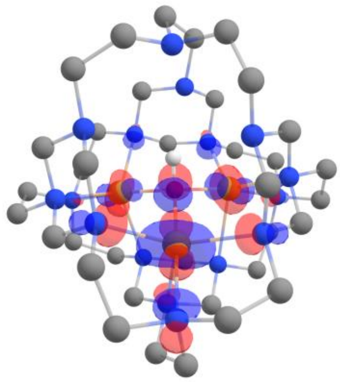
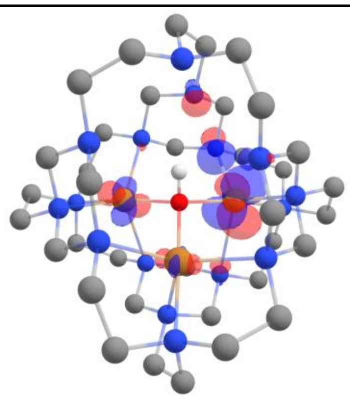
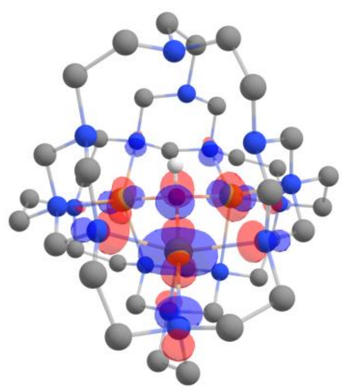
Transitions (nm)	Donor orbital	Acceptor orbital
554 nm		
756 nm		
851 nm		

Table S6: Selected TD-DFT transitions for **4c**. Orbitals plotted at a 0.048 isosurface value.

Complex/ox. st.	$Cu^{I}Cu^{I}Cu^{I}$	$Cu^{II}Cu^{I}Cu^{I}$	$Cu^{II}Cu^{II}Cu^{I}$	$Cu^{II}Cu^{II}Cu^{II}$
3	**Cu-O: 1.90 Å;** **Cu-N: 2.64 Å;** **Cu···Cu: 2.68 Å**	Cu-O: 1.88 Å; Cu-N: 2.40 Å; Cu···Cu: 3.07 Å	Cu-O: 1.90 Å; Cu-N: 2.29 Å; Cu···Cu: 3.15 Å	Cu-O: 1.93 Å; Cu-N: 2.23 Å; Cu···Cu: 3.17 Å
4	Cu-O: 1.96 Å; Cu-N: 2.47 Å; Cu···Cu: 3.19 Å	Cu-O: 1.99 Å; Cu-N: 2.36 Å; Cu···Cu: 3.29 Å	Cu-O: 2.01 Å; Cu-N: 2.29 Å; Cu···Cu: 3.35 Å	Cu-O: 2.03 Å; Cu-N: 2.26 Å; Cu···Cu: 3.36 Å

Table S7. Comparison of geometry of optimized **3** and **4** at different oxidation states.

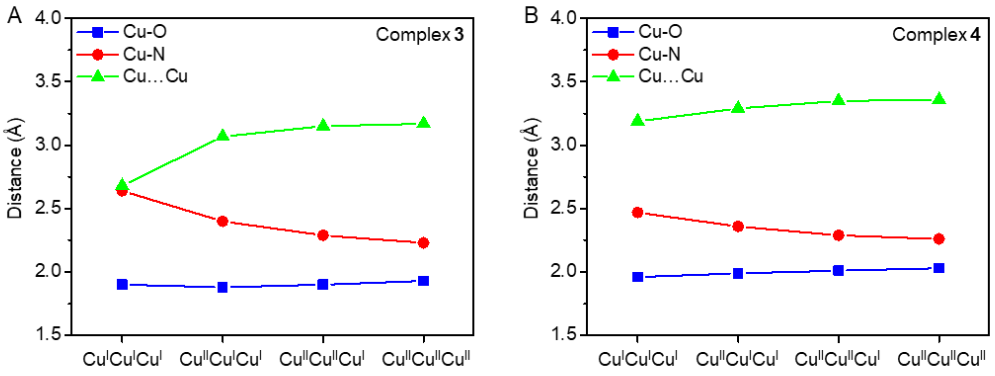


Fig. S23. Selected average bond distances from the optimized geometries of (A) **3** and (B) **4** at different oxidation states.

Cartesian coordinates of complexes used in computations

<u>Complex – Level of theory optimized (Calculations used for)</u>
Charge, spin multiplicity

<u>[**TREN**$_4$Cu^{I}Cu^{I}Cu^I(μ_3-OH)] – BP86/def2-SVP (C, H, O, N)/def2-TZVP (Cu)</u>
2, 1

29	9.733391000	-0.179256000	10.360415000
6	10.982866000	2.011531000	12.156563000
1	11.025418000	2.878547000	12.864461000
1	12.009104000	1.913309000	11.746150000
6	8.394227000	-1.447503000	12.936769000
1	7.985615000	-2.246915000	13.606288000
1	8.085973000	-0.488172000	13.402451000
7	7.805923000	-1.495428000	11.593444000
6	9.919155000	-1.572553000	12.945956000
1	10.265463000	-1.593725000	14.006910000
1	10.208664000	-2.549079000	12.510799000
7	10.642610000	-0.508729000	12.190831000
7	11.791656000	-1.584373000	9.582177000
7	12.160309000	-0.182954000	7.675744000
7	11.009843000	-2.284982000	7.415317000
6	10.621100000	0.765416000	12.970879000
1	11.315256000	0.693894000	13.841371000
1	9.607250000	0.884495000	13.400234000
6	11.554433000	-2.725960000	8.702771000
1	10.826684000	-3.402991000	9.196248000
1	12.509034000	-3.313851000	8.540103000
6	7.797845000	-2.849105000	11.039747000
1	7.209797000	-3.545175000	11.712482000
1	8.837605000	-3.232061000	10.990502000
6	12.060197000	-0.937458000	11.985616000
1	12.484165000	-1.318461000	12.944471000
1	12.653522000	-0.038392000	11.728707000
6	11.916571000	-1.311899000	6.791432000
1	11.444677000	-0.951305000	5.856688000
1	12.892217000	-1.815181000	6.504521000

6	12.715981000	-0.648758000	8.934966000
1	12.873972000	0.226339000	9.596813000
1	13.725895000	-1.145574000	8.790588000
6	12.365345000	1.643691000	5.927806000
1	12.066134000	0.948454000	5.119042000
1	13.170375000	2.282705000	5.475675000
6	12.254622000	-2.006231000	10.906266000
1	13.334921000	-2.299115000	10.907353000
1	11.699070000	-2.927608000	11.179993000
6	13.013790000	0.840734000	7.063088000
1	13.325627000	1.529292000	7.875897000
1	13.965855000	0.403484000	6.662554000
29	8.570128000	-1.616729000	7.759195000
6	10.759997000	-3.415140000	6.512144000
1	11.626383000	-4.123852000	6.470437000
1	10.663181000	-3.004541000	5.485846000
6	7.297324000	-4.191754000	9.096962000
1	6.496666000	-4.860431000	9.504539000
1	8.255761000	-4.658520000	9.406361000
7	7.250146000	-2.848421000	9.685257000
6	7.173981000	-4.200765000	7.571885000
1	7.152001000	-5.261691000	7.225534000
1	6.198205000	-3.764556000	7.281421000
7	8.239397000	-3.446797000	6.849592000
7	7.167663000	-0.837004000	5.699587000
7	8.571409000	1.068012000	5.332419000
7	6.468452000	1.330575000	6.480667000
6	9.512660000	-4.228235000	6.872456000
1	9.440986000	-5.098560000	6.178108000
1	9.630089000	-4.657821000	7.886400000
6	6.026716000	0.043544000	5.935708000
1	5.348495000	-0.449201000	6.662854000
1	5.439820000	0.206719000	4.980574000
6	5.897063000	-2.293234000	9.691639000
1	5.199485000	-2.965411000	10.278559000
1	5.515566000	-2.243293000	8.651368000
6	7.812398000	-3.241093000	5.431568000
1	7.430813000	-4.199527000	5.007176000
1	8.712370000	-2.985166000	4.839186000
6	7.443065000	1.953449000	5.574906000
1	7.804023000	2.887907000	6.047085000
1	6.941071000	2.240711000	4.598702000
6	8.104871000	-0.190704000	4.776215000
1	8.979431000	-0.853455000	4.619068000
1	7.609227000	-0.045760000	3.765810000
6	10.400064000	2.814039000	5.129437000
1	9.705361000	3.623515000	5.427949000
1	11.040438000	3.265569000	4.325145000
6	6.744938000	-2.160632000	5.236071000
1	6.453228000	-2.161334000	4.155458000
1	5.822680000	-2.433456000	5.790602000
6	9.596610000	1.679672000	4.480024000
1	10.284614000	0.866169000	4.168776000
1	9.160726000	2.080752000	3.527569000
29	7.133732000	0.985916000	8.921374000

8	8.864795000	0.114946000	8.628418000
6	5.338977000	2.234920000	6.729351000
1	4.631238000	2.277421000	5.862207000
1	5.750538000	3.260785000	6.826652000
6	4.555728000	-0.349247000	10.191094000
1	3.885707000	-0.756137000	10.990979000
1	4.089734000	-0.658122000	9.232121000
7	5.898404000	-0.938916000	10.239760000
6	4.548128000	1.175837000	10.314442000
1	3.487539000	1.523286000	10.335069000
1	4.983412000	1.465885000	11.290749000
7	5.304154000	1.897357000	9.249956000
7	7.914007000	3.044624000	10.324605000
7	9.820901000	3.409892000	8.922948000
7	10.080044000	2.261255000	11.026109000
6	4.524155000	1.875382000	7.975786000
1	3.654443000	2.570607000	8.046523000
1	4.093660000	0.861886000	7.857809000
6	8.793068000	2.807526000	11.466465000
1	8.298766000	2.080822000	12.144011000
1	8.956602000	3.762412000	12.053660000
6	6.452076000	-0.946087000	11.593432000
1	5.778675000	-1.532507000	12.290236000
1	6.502607000	0.094087000	11.975118000
7	11.190965000	2.436277000	6.304654000
6	5.510863000	3.315137000	9.677308000
1	4.552460000	3.740484000	10.057906000
1	5.768349000	3.907361000	8.777676000
6	10.704860000	3.166496000	10.052221000
1	11.639265000	2.693447000	9.692246000
1	10.992563000	4.142349000	10.554636000
6	8.562235000	3.967362000	9.388103000
1	7.900606000	4.125176000	8.512814000
1	8.707665000	4.977604000	9.883931000
6	11.569065000	3.611045000	7.096077000
1	12.377493000	3.311640000	7.791626000
1	12.022140000	4.414918000	6.456272000
6	6.590379000	3.509413000	10.745946000
1	6.590425000	4.589988000	11.037810000
1	6.316022000	2.954997000	11.667822000
6	10.434482000	4.261588000	7.898321000
1	9.622012000	4.573522000	7.209407000
1	10.836021000	5.213710000	8.334511000
1	9.434252000	0.683367000	8.059623000

[**TREN**$_4$Cu^{I}Cu^{I}Cu^{II}(μ_3-OH)] – BP86/def2-SVP (C, H, O, N)/def2-TZVP (Cu)

3, 2

29	9.867699000	-0.252278000	10.297176000
6	11.003535000	1.970426000	12.057747000
1	11.027273000	2.896362000	12.683653000
1	12.024885000	1.869689000	11.635057000
6	8.397633000	-1.340594000	12.894941000
1	7.894433000	-2.111376000	13.528052000
1	8.098392000	-0.362154000	13.324360000
7	7.909043000	-1.372691000	11.499656000

6	9.907769000	-1.530610000	13.016478000
1	10.185168000	-1.512097000	14.095906000
1	10.190401000	-2.537853000	12.651056000
7	10.696260000	-0.522880000	12.255915000
7	11.658692000	-1.548835000	9.652030000
7	12.068763000	-0.138308000	7.751116000
7	10.860800000	-2.234046000	7.451121000
6	10.699457000	0.785005000	12.971991000
1	11.440417000	0.775505000	13.804403000
1	9.713253000	0.918153000	13.456622000
6	11.408508000	-2.684620000	8.746904000
1	10.690042000	-3.373686000	9.232315000
1	12.365953000	-3.249867000	8.576365000
6	7.897300000	-2.740753000	10.972296000
1	7.256819000	-3.402649000	11.623795000
1	8.924484000	-3.155875000	10.987740000
6	12.091369000	-1.009883000	12.057090000
1	12.498026000	-1.443772000	12.999191000
1	12.732425000	-0.137420000	11.822924000
6	11.785443000	-1.238275000	6.845599000
1	11.309599000	-0.844782000	5.928537000
1	12.734381000	-1.767282000	6.538872000
6	12.629431000	-0.645323000	8.988749000
1	12.860459000	0.205856000	9.658056000
1	13.593307000	-1.210179000	8.821449000
6	12.375517000	1.654369000	5.969708000
1	12.108602000	0.953654000	5.154203000
1	13.204196000	2.280823000	5.548643000
6	12.195466000	-2.049727000	10.942542000
1	13.257632000	-2.374651000	10.846843000
1	11.622521000	-2.960662000	11.213506000
6	12.966919000	0.863844000	7.142286000
1	13.263991000	1.560859000	7.952600000
1	13.918938000	0.393563000	6.787675000
29	8.693098000	-1.653489000	7.762670000
6	10.734697000	-3.376168000	6.505207000
1	11.657575000	-4.003152000	6.497111000
1	10.654784000	-2.945198000	5.486202000
6	7.408799000	-4.161876000	9.099819000
1	6.620123000	-4.776445000	9.597903000
1	8.376452000	-4.613473000	9.402750000
7	7.404152000	-2.765305000	9.589209000
6	7.221567000	-4.269832000	7.589235000
1	7.220524000	-5.346285000	7.300868000
1	6.224394000	-3.880469000	7.306773000
7	8.245960000	-3.517862000	6.815302000
7	7.207595000	-0.861474000	5.842430000
7	8.616212000	1.027267000	5.412652000
7	6.542923000	1.340993000	6.650146000
6	9.532085000	-4.272614000	6.791161000
1	9.500306000	-5.087777000	6.031746000
1	9.656925000	-4.779218000	7.767849000
6	6.083012000	0.035820000	6.120847000
1	5.422322000	-0.448092000	6.867709000
1	5.474328000	0.209777000	5.187999000

6	6.044128000	-2.207727000	9.560324000
1	5.347658000	-2.870012000	10.152354000
1	5.672842000	-2.187900000	8.516808000
6	7.757923000	-3.271289000	5.427238000
1	7.327802000	-4.204184000	4.995779000
1	8.632342000	-3.020866000	4.794885000
6	7.521173000	1.935401000	5.701109000
1	7.919352000	2.861565000	6.155790000
1	6.975306000	2.227476000	4.755882000
6	8.095749000	-0.211396000	4.863525000
1	8.943494000	-0.884700000	4.628726000
1	7.530443000	-0.040758000	3.897952000
6	10.414946000	2.787609000	5.096288000
1	9.725676000	3.616420000	5.351278000
1	11.060921000	3.194888000	4.275908000
6	6.713569000	-2.157303000	5.337840000
1	6.366249000	-2.087150000	4.278590000
1	5.812764000	-2.430868000	5.926270000
6	9.610004000	1.626828000	4.503998000
1	10.296094000	0.810506000	4.196426000
1	9.135869000	1.989436000	3.556522000
29	7.153099000	1.134582000	8.851469000
8	8.852851000	0.142821000	8.617909000
6	5.395216000	2.279248000	6.765410000
1	4.781077000	2.285551000	5.833364000
1	5.815684000	3.301998000	6.856736000
6	4.616964000	-0.351698000	10.058400000
1	3.987080000	-0.862990000	10.827099000
1	4.186235000	-0.645259000	9.078350000
7	6.013546000	-0.838008000	10.086433000
6	4.486469000	1.155570000	10.260945000
1	3.405054000	1.424722000	10.263047000
1	4.868105000	1.433780000	11.262714000
7	5.222904000	1.957218000	9.246379000
7	7.858852000	2.892031000	10.236735000
7	9.761280000	3.354026000	8.853719000
7	10.073115000	2.108180000	10.914385000
6	4.483128000	1.977992000	7.952198000
1	3.658961000	2.727357000	7.978183000
1	3.989868000	0.996219000	7.817485000
6	8.762336000	2.598128000	11.367512000
1	8.280965000	1.827063000	12.001725000
1	8.891879000	3.526435000	11.993690000
6	6.544982000	-0.831439000	11.454951000
1	5.868848000	-1.424741000	12.137154000
1	6.569121000	0.208091000	11.837911000
7	11.189520000	2.451746000	6.295688000
6	5.445366000	3.344641000	9.746261000
1	4.514042000	3.754980000	10.199241000
1	5.673587000	3.992072000	8.876993000
6	10.665487000	3.064931000	9.954255000
1	11.595177000	2.616441000	9.556937000
1	10.953696000	4.013902000	10.497746000
6	8.521133000	3.894837000	9.369944000
1	7.853624000	4.152111000	8.523929000

1	8.682614000	4.840931000	9.967295000
6	11.532594000	3.651025000	7.067082000
1	12.352925000	3.392721000	7.765211000
1	11.952146000	4.464528000	6.420426000
6	6.578374000	3.420591000	10.767405000
1	6.683214000	4.474788000	11.115915000
1	6.317423000	2.830500000	11.670706000
6	10.368209000	4.256558000	7.859115000
1	9.558553000	4.562678000	7.164755000
1	10.732632000	5.204324000	8.330877000
1	9.437600000	0.695093000	8.040209000

[**TREN4**$Cu^ICu^{II}Cu^{II}$(μ_3-OH)] – BP86/def2-SVP (C, H, O, N)/def2-TZVP (Cu)

4, 3

29	11.332640000	5.553828000	4.694543000
29	8.952332000	7.914458000	4.637590000
29	10.782927000	7.404710000	7.407496000
8	10.728126000	7.341804000	5.391253000
7	9.616170000	4.313948000	5.914762000
7	7.004834000	8.315041000	3.891774000
7	13.394214000	5.563578000	5.638601000
7	9.573611000	7.906073000	2.464139000
7	8.574436000	9.821341000	5.864378000
7	13.886588000	7.900561000	6.183297000
7	10.804451000	10.644345000	5.480747000
7	11.830757000	3.593115000	4.060469000
7	8.833007000	5.877654000	7.609103000
7	12.839213000	6.498805000	7.837149000
7	12.019460000	8.043439000	2.452275000
7	10.265118000	9.597520000	7.628435000
7	7.817044000	5.871880000	5.392870000
7	10.594959000	7.343738000	9.526794000
7	13.504869000	10.147592000	4.106372000
7	10.957021000	5.878678000	2.436908000
6	8.835050000	9.819209000	7.318437000
6	14.290863000	6.735941000	5.412774000
6	13.288827000	5.305476000	7.092956000
6	13.835220000	7.575184000	7.596097000
6	9.698170000	6.508902000	1.987735000
6	10.777854000	8.682734000	2.046360000
6	6.012640000	7.400587000	4.528065000
6	8.359487000	4.518423000	5.173840000
6	12.083854000	6.696276000	1.917933000
6	7.590734000	6.059726000	6.837337000
6	9.355609000	4.526975000	7.350487000
6	8.503107000	6.040485000	9.051917000
6	12.071523000	3.643784000	2.587335000
6	13.201521000	8.815396000	1.994154000
6	11.093595000	10.607811000	6.905784000
6	9.394515000	10.906608000	5.265402000
6	9.728237000	6.202649000	9.940708000
6	14.804505000	9.641065000	4.556455000
6	11.029381000	4.498088000	1.873197000
6	7.122886000	10.090878000	5.640837000
6	14.025511000	4.384434000	4.962994000

6	10.096522000	2.914800000	5.741302000
6	8.387213000	8.559616000	1.824149000
6	6.687721000	9.736890000	4.222843000
6	10.713885000	2.654776000	4.373085000
6	13.070987000	3.208299000	4.797203000
6	14.803893000	9.045918000	5.967806000
6	9.999058000	8.646347000	9.949359000
6	13.380647000	10.186747000	2.646942000
6	10.500611000	9.801858000	9.093397000
6	12.783744000	6.163184000	9.291537000
6	11.616003000	11.672958000	4.787665000
6	11.972247000	7.182603000	10.082720000
6	6.526706000	5.971951000	4.652861000
6	13.124556000	11.409593000	4.747042000
6	7.058303000	8.104733000	2.414860000
1	8.506616000	10.800415000	7.754380000
1	8.227064000	9.023886000	7.791557000
1	15.343677000	6.426068000	5.667487000
1	14.261605000	6.980916000	4.334870000
1	12.574482000	4.479076000	7.271503000
1	14.287880000	4.979723000	7.486616000
1	14.833021000	7.235759000	7.996032000
1	13.551352000	8.481469000	8.166584000
1	8.845310000	5.914583000	2.369506000
1	9.653207000	6.489019000	0.865855000
1	10.738570000	8.818177000	0.928580000
1	10.712752000	9.685019000	2.508925000
1	5.757955000	7.807589000	5.525189000
1	5.060454000	7.395728000	3.951232000
1	8.543089000	4.379793000	4.091310000
1	7.602564000	3.747940000	5.488227000
1	12.046079000	6.681882000	0.791766000
1	13.044404000	6.234675000	2.219560000
1	6.804504000	5.339345000	7.197215000
1	7.209872000	7.082919000	7.021368000
1	8.626844000	3.755145000	7.725237000
1	10.303066000	4.384040000	7.903980000
1	7.845622000	6.929030000	9.138998000
1	7.898442000	5.182251000	9.430852000
1	13.086094000	4.051268000	2.413061000
1	12.074660000	2.619338000	2.151296000
1	14.092417000	8.184021000	2.193298000
1	13.181917000	8.963118000	0.885876000
1	12.156686000	10.343830000	7.060260000
1	10.917405000	11.613405000	7.383054000
1	9.198961000	10.962388000	4.177053000
1	9.067996000	11.889146000	5.711576000
1	10.339780000	5.280190000	9.929871000
1	9.395455000	6.329360000	10.995940000
1	15.161185000	8.883082000	3.830312000
1	15.591271000	10.436886000	4.542670000
1	10.022605000	4.040016000	1.959712000
1	11.258420000	4.519021000	0.783092000
1	6.552078000	9.494770000	6.381694000
1	6.872501000	11.156352000	5.847511000

1	14.388944000	4.730429000	3.974436000
1	14.930444000	4.044831000	5.516919000
1	10.841042000	2.722993000	6.541054000
1	9.275600000	2.178762000	5.910135000
1	8.511683000	9.653926000	1.956454000
1	8.379043000	8.382026000	0.723993000
1	7.195414000	10.389454000	3.486818000
1	5.598554000	9.934933000	4.107727000
1	9.947300000	2.745598000	3.578558000
1	11.066117000	1.599279000	4.329151000
1	12.777550000	2.805487000	5.786229000
1	13.598017000	2.377566000	4.276849000
1	14.518914000	9.825346000	6.704656000
1	15.858601000	8.770031000	6.218640000
1	8.896704000	8.565593000	9.886837000
1	10.226546000	8.853989000	11.018822000
1	12.528515000	10.843787000	2.380281000
1	14.268442000	10.667286000	2.162961000
1	11.592815000	9.936321000	9.229864000
1	10.029899000	10.748472000	9.445195000
1	12.339611000	5.151680000	9.388175000
1	13.805940000	6.088720000	9.727725000
1	11.217674000	11.752276000	3.754436000
1	11.461469000	12.683710000	5.241020000
1	12.470747000	8.170875000	10.066564000
1	11.931136000	6.876909000	11.151928000
1	6.685430000	5.532871000	3.646291000
1	5.735261000	5.347644000	5.130849000
1	13.537194000	11.423297000	5.775666000
1	13.593460000	12.292298000	4.244279000
1	6.888812000	7.030500000	2.206111000
1	6.227002000	8.643700000	1.907658000
1	11.389142000	8.004095000	5.055192000

[**TREN**$_4$Cu^{II}Cu^{II}Cu^{II}(μ_3-OH)] – BP86/def2-SVP (C, H, O, N)/def2-TZVP (Cu)

5, 4

29	11.301151000	5.508161000	4.709651000
29	8.903489000	7.865459000	4.645166000
29	10.722745000	7.370986000	7.437181000
8	10.694486000	7.306051000	5.410588000
7	9.618399000	4.319254000	5.887529000
7	6.996634000	8.310187000	3.889444000
7	13.377816000	5.553089000	5.634479000
7	9.552486000	7.893690000	2.467821000
7	8.593633000	9.796404000	5.842628000
7	13.862294000	7.908986000	6.131074000
7	10.854487000	10.602551000	5.492701000
7	11.830244000	3.585372000	4.063099000
7	8.859758000	5.878794000	7.614952000
7	12.814083000	6.523291000	7.822579000
7	12.000379000	8.079358000	2.489587000
7	10.255405000	9.578153000	7.643132000
7	7.812549000	5.898759000	5.399239000
7	10.589229000	7.339924000	9.535021000
7	13.620621000	10.258882000	4.061893000

7	10.970441000	5.882876000	2.466246000
6	8.832210000	9.810266000	7.303379000
6	14.276423000	6.720493000	5.392861000
6	13.272453000	5.319934000	7.094449000
6	13.794148000	7.611253000	7.556015000
6	9.707930000	6.497074000	1.996057000
6	10.747170000	8.685337000	2.051032000
6	5.993844000	7.419421000	4.552346000
6	8.351822000	4.541503000	5.160791000
6	12.096001000	6.720507000	1.970371000
6	7.607095000	6.073630000	6.852980000
6	9.371399000	4.523443000	7.331839000
6	8.521326000	6.007407000	9.069474000
6	12.098997000	3.650799000	2.591252000
6	13.168953000	8.855754000	1.997821000
6	11.097638000	10.584347000	6.931801000
6	9.442770000	10.856371000	5.234452000
6	9.745860000	6.177306000	9.953586000
6	14.861752000	9.636736000	4.520959000
6	11.065947000	4.507318000	1.873209000
6	7.144991000	10.111131000	5.607377000
6	14.019940000	4.359063000	4.982068000
6	10.072126000	2.901686000	5.710231000
6	8.357212000	8.523320000	1.806312000
6	6.706545000	9.747078000	4.195734000
6	10.701046000	2.646225000	4.348936000
6	13.059690000	3.190254000	4.819488000
6	14.820357000	9.026721000	5.927756000
6	9.967253000	8.633301000	9.962204000
6	13.369843000	10.240853000	2.621560000
6	10.463476000	9.796155000	9.117080000
6	12.797496000	6.202098000	9.288918000
6	11.654795000	11.665491000	4.830718000
6	11.977964000	7.210170000	10.081040000
6	6.495219000	5.989398000	4.686737000
6	13.171351000	11.444951000	4.789617000
6	7.037636000	8.069668000	2.413013000
1	8.508926000	10.800196000	7.718658000
1	8.205312000	9.031985000	7.778967000
1	15.324063000	6.418063000	5.670081000
1	14.267870000	6.935830000	4.307913000
1	12.566117000	4.490464000	7.287448000
1	14.272463000	5.008625000	7.493584000
1	14.792968000	7.297930000	7.969270000
1	13.491015000	8.525300000	8.103278000
1	8.856022000	5.888043000	2.355199000
1	9.687398000	6.477461000	0.874920000
1	10.722124000	8.795172000	0.931401000
1	10.650298000	9.699159000	2.483289000
1	5.751346000	7.845699000	5.544398000
1	5.038547000	7.422826000	3.980881000
1	8.519672000	4.409830000	4.075362000
1	7.595161000	3.776211000	5.479077000
1	12.085309000	6.698181000	0.845552000
1	13.055827000	6.275007000	2.295823000

1	6.829393000	5.348723000	7.214110000
1	7.224807000	7.093123000	7.051299000
1	8.637174000	3.757307000	7.699446000
1	10.319427000	4.361321000	7.878288000
1	7.846732000	6.881055000	9.169936000
1	7.933085000	5.130380000	9.426988000
1	13.117751000	4.055839000	2.436761000
1	12.108880000	2.627988000	2.151809000
1	14.070634000	8.232444000	2.166606000
1	13.119539000	9.006193000	0.891484000
1	12.158634000	10.339851000	7.127607000
1	10.893751000	11.593098000	7.386678000
1	9.273697000	10.880769000	4.140515000
1	9.113031000	11.852484000	5.641268000
1	10.373369000	5.265448000	9.939820000
1	9.420168000	6.300017000	11.011338000
1	15.181275000	8.887131000	3.771731000
1	15.680225000	10.400246000	4.529983000
1	10.060435000	4.042998000	1.929688000
1	11.315294000	4.555066000	0.789218000
1	6.553782000	9.549425000	6.358418000
1	6.932536000	11.187571000	5.795587000
1	14.401587000	4.690220000	3.995369000
1	14.913651000	4.024261000	5.555624000
1	10.800654000	2.689537000	6.519089000
1	9.231874000	2.186190000	5.863830000
1	8.472834000	9.621884000	1.905980000
1	8.350827000	8.315235000	0.712243000
1	7.223312000	10.377372000	3.447123000
1	5.620611000	9.958379000	4.074671000
1	9.948116000	2.741403000	3.542121000
1	11.055734000	1.591824000	4.301400000
1	12.752499000	2.792506000	5.806355000
1	13.579453000	2.351309000	4.305175000
1	14.569007000	9.809911000	6.671527000
1	15.865850000	8.715084000	6.172608000
1	8.866719000	8.535853000	9.894758000
1	10.187271000	8.832129000	11.034864000
1	12.509626000	10.903013000	2.404534000
1	14.234751000	10.709961000	2.087121000
1	11.550175000	9.951083000	9.270589000
1	9.970050000	10.735305000	9.455059000
1	12.385645000	5.179515000	9.407572000
1	13.830363000	6.158489000	9.702668000
1	11.260870000	11.777634000	3.799891000
1	11.488434000	12.659937000	5.313237000
1	12.455598000	8.208480000	10.060456000
1	11.945307000	6.909351000	11.151773000
1	6.623884000	5.526484000	3.687065000
1	5.717458000	5.378624000	5.200412000
1	13.599856000	11.417236000	5.809515000
1	13.612769000	12.359634000	4.319886000
1	6.868105000	6.991516000	2.226900000
1	6.196751000	8.596785000	1.909255000
1	11.353151000	7.971043000	5.077297000

[**TREN**$_3$Cu^{I}Cu^{I}Cu^{I}(μ_3-O)] – BP86/def2-SVP (C, H, O, N)/def2-TZVP (Cu)

1, 1

29	5.142650000	1.378498000	-2.485868000
7	3.599546000	0.008147000	-3.843059000
6	3.990698000	-1.387176000	-4.160881000
1	3.978414000	-1.951726000	-3.207063000
1	3.219284000	-1.865609000	-4.818215000
6	5.376240000	-1.559008000	-4.822788000
7	6.541422000	-1.138282000	-4.048112000
7	4.964341000	2.630356000	-4.157060000
6	6.092672000	2.376960000	-5.090235000
7	7.353769000	2.666930000	-4.438305000
29	7.828423000	1.225693000	-2.215122000
29	6.425283000	2.750381000	-0.553633000
7	8.102229000	2.913058000	1.158071000
6	9.397202000	2.523003000	0.606058000
7	9.590117000	3.168400000	-0.690685000
7	8.019221000	-1.650082000	-2.143339000
6	6.992811000	-2.122506000	-3.028362000
1	7.365468000	-3.018277000	-3.577727000
6	9.378642000	-1.464161000	-2.607531000
1	10.038602000	-1.381079000	-1.717510000
1	9.702238000	-2.399838000	-3.117526000
6	9.704348000	-0.330805000	-3.615446000
7	9.615471000	1.088967000	-3.108933000
7	3.431167000	0.968776000	-0.963684000
6	2.670818000	-0.161950000	-1.502907000
6	2.382393000	0.024713000	-2.999854000
6	3.436626000	0.839124000	-5.048152000
6	3.657952000	2.337684000	-4.792640000
6	5.024547000	4.052453000	-3.727967000
7	6.306979000	4.333104000	-3.109331000
7	6.019713000	4.703153000	0.000640000
6	7.288307000	5.213551000	0.610700000
6	7.928909000	4.281807000	1.653748000
1	7.307731000	4.248954000	2.572124000
1	8.898871000	4.742375000	1.953238000
1	8.018073000	5.352614000	-0.209391000
1	7.102698000	6.210630000	1.079788000
6	5.589128000	5.639778000	-1.082133000
1	4.530763000	5.421776000	-1.315712000
1	5.614007000	6.687429000	-0.698321000
6	6.398842000	5.597468000	-2.387776000
6	7.409534000	4.064221000	-4.018247000
6	8.523139000	2.167299000	-5.156171000
6	9.763411000	2.022637000	-4.266181000
6	10.720835000	1.335230000	-2.118604000
1	11.701259000	1.177405000	-2.631137000
1	10.636943000	0.550397000	-1.342453000
6	10.757520000	2.732853000	-1.449388000
1	10.989795000	3.508161000	-2.211220000
1	11.640614000	2.728210000	-0.773416000
1	10.042187000	3.016056000	-3.865870000
1	10.618544000	1.697192000	-4.904163000

1	8.245291000	1.181218000	-5.580434000
1	8.810377000	2.814214000	-6.024716000
1	7.387733000	4.748832000	-4.921638000
1	8.361956000	4.255848000	-3.484554000
1	7.473168000	5.781890000	-2.181307000
1	6.057572000	6.471722000	-3.002010000
6	4.948621000	4.583566000	1.049449000
6	3.520463000	4.291071000	0.527384000
7	3.443022000	3.315145000	-0.551065000
6	2.673733000	2.083071000	-0.389903000
1	1.697903000	2.137872000	-0.927489000
1	3.041779000	5.253365000	0.227229000
1	2.934171000	3.946168000	1.410304000
1	5.268681000	3.773304000	1.735068000
1	4.903468000	5.527165000	1.646469000
1	4.845230000	4.715310000	-4.626387000
1	4.206825000	4.217132000	-2.998028000
1	2.876471000	2.733702000	-4.111734000
1	3.548452000	2.883444000	-5.761841000
1	4.156277000	0.487475000	-5.812418000
1	2.427052000	0.714672000	-5.513324000
1	1.877988000	1.004620000	-3.130216000
1	1.653247000	-0.750199000	-3.345697000
1	3.266505000	-1.084458000	-1.347266000
1	1.705036000	-0.325737000	-0.970150000
1	8.996217000	-0.425977000	-4.460843000
1	10.739428000	-0.490171000	-4.006190000
1	9.378883000	1.405135000	0.559092000
1	5.942230000	3.005764000	-6.017285000
1	6.088833000	1.313699000	-5.390434000
1	5.381959000	-1.047005000	-5.812345000
1	5.484248000	-2.637526000	-5.071007000
1	6.145900000	-2.475116000	-2.387543000
1	2.421810000	1.915663000	0.692100000
1	10.254150000	2.816707000	1.264903000
1	6.313646000	-0.256422000	-3.539311000
1	7.681873000	-0.940863000	-1.473599000
1	7.801250000	2.218795000	1.847391000
1	4.387904000	3.047541000	-0.904278000
1	4.187634000	0.661089000	-0.335684000
1	8.721686000	2.981075000	-1.242204000
8	6.405816000	0.936532000	-1.057821000

[**TREN**$_3$Cu^{I}Cu^{I}Cu^{II}(μ_3-O)] – BP86/def2-SVP (C, H, O, N)/def2-TZVP (Cu)

2, 2

29	5.113601000	0.579796000	-2.423412000
7	3.416344000	0.075222000	-3.714160000
6	3.495152000	-1.378380000	-4.024000000
1	3.120133000	-1.935554000	-3.142043000
1	2.816326000	-1.641528000	-4.869412000
6	4.909727000	-1.851175000	-4.339291000
7	5.832736000	-1.508324000	-3.244264000
7	5.108129000	2.608988000	-4.112997000
6	6.257924000	2.349894000	-4.977066000
7	7.510572000	2.550797000	-4.246704000

29	8.041408000	0.982797000	-2.282325000
29	6.197588000	2.922971000	-0.652406000
7	7.960702000	3.116538000	0.816342000
6	9.332713000	3.219660000	0.287810000
7	9.685306000	2.091716000	-0.551806000
7	8.177109000	-1.228943000	-2.634919000
6	7.221777000	-1.808268000	-3.587275000
1	7.423134000	-1.369017000	-4.586354000
6	9.579668000	-1.467009000	-3.031345000
1	10.195712000	-1.518237000	-2.112721000
1	9.715593000	-2.445852000	-3.547367000
6	10.077503000	-0.346307000	-3.949980000
7	9.966616000	0.993277000	-3.312555000
7	3.247547000	0.661011000	-0.804892000
6	2.182785000	-0.053394000	-1.518208000
6	2.141107000	0.349639000	-2.998236000
6	3.499469000	0.867374000	-4.971369000
6	3.823667000	2.352022000	-4.775912000
6	5.167724000	3.974925000	-3.598192000
7	6.412325000	4.201743000	-2.857734000
7	5.837123000	4.983253000	0.037104000
6	7.049690000	5.410806000	0.783833000
6	7.613920000	4.280532000	1.651187000
1	6.869512000	3.961764000	2.407415000
1	8.488825000	4.668101000	2.224485000
1	7.816652000	5.722979000	0.048223000
1	6.836477000	6.307252000	1.411893000
6	5.589354000	5.854755000	-1.140211000
1	4.531337000	5.723427000	-1.444106000
1	5.690881000	6.931529000	-0.863213000
6	6.506316000	5.574413000	-2.334178000
6	7.564875000	3.914160000	-3.715853000
6	8.665976000	2.242506000	-5.101902000
6	9.981924000	2.069900000	-4.337590000
6	11.097106000	1.177532000	-2.358460000
1	12.049648000	1.348278000	-2.913336000
1	11.229850000	0.227371000	-1.802579000
6	10.893408000	2.303608000	-1.347499000
1	10.790457000	3.279942000	-1.869720000
1	11.827555000	2.388276000	-0.739229000
1	10.242536000	3.017880000	-3.827836000
1	10.795971000	1.894090000	-5.080196000
1	8.426684000	1.311063000	-5.657815000
1	8.829908000	3.025997000	-5.885052000
1	7.619776000	4.659223000	-4.567470000
1	8.482997000	4.032831000	-3.107042000
1	7.564608000	5.742334000	-2.042938000
1	6.285718000	6.337727000	-3.122611000
6	4.666726000	5.005429000	0.955084000
6	3.500727000	4.151708000	0.474930000
7	3.916938000	2.763691000	0.228313000
6	2.831496000	1.993803000	-0.382548000
1	2.504994000	2.554544000	-1.284050000
1	3.091050000	4.551674000	-0.476791000
1	2.671396000	4.237765000	1.217762000

1	4.999807000	4.627422000	1.941980000
1	4.319338000	6.050867000	1.126593000
1	5.073846000	4.727580000	-4.439807000
1	4.305885000	4.127217000	-2.918109000
1	3.034614000	2.828322000	-4.157974000
1	3.760639000	2.847610000	-5.777948000
1	4.270325000	0.401324000	-5.617324000
1	2.542922000	0.791906000	-5.541001000
1	1.932577000	1.435111000	-3.072406000
1	1.289200000	-0.164334000	-3.502281000
1	2.364921000	-1.142484000	-1.416782000
1	1.169362000	0.125532000	-1.082040000
1	9.470602000	-0.337442000	-4.876211000
1	11.126403000	-0.552993000	-4.266366000
1	10.057667000	3.375725000	1.134176000
1	6.221299000	3.014399000	-5.893976000
1	6.226661000	1.299093000	-5.327240000
1	5.287698000	-1.362486000	-5.261776000
1	4.878045000	-2.943684000	-4.561083000
1	7.385530000	-2.913843000	-3.686546000
1	1.933267000	1.948144000	0.295040000
1	9.392372000	4.135648000	-0.338268000
1	5.570300000	-2.048211000	-2.405646000
1	8.005272000	-1.619660000	-1.699077000
1	7.877202000	2.250259000	1.363614000
1	4.173965000	2.325360000	1.125457000
1	3.568837000	0.114865000	0.003371000
1	9.789111000	1.242538000	0.020631000
8	6.474696000	1.163979000	-1.251286000

[**TREN**$_3$Cu^{I}Cu^{II}Cu^{II}(μ_3-O)] – BP86/def2-SVP (C, H, O, N)/def2-TZVP (Cu)

3, 3

29	5.013514000	0.642931000	-2.445526000
7	3.370342000	0.079773000	-3.764293000
6	3.501299000	-1.367388000	-4.095789000
1	3.095849000	-1.957383000	-3.249704000
1	2.879667000	-1.632801000	-4.981157000
6	4.947675000	-1.768680000	-4.339857000
7	5.804839000	-1.386192000	-3.189495000
7	5.091639000	2.552374000	-4.021035000
6	6.245253000	2.285569000	-4.893939000
7	7.515811000	2.492293000	-4.178846000
29	8.129092000	1.094591000	-2.239055000
29	6.158894000	2.985397000	-0.669338000
7	7.848373000	3.055874000	0.768780000
6	9.206555000	3.135575000	0.207034000
7	9.548084000	2.012951000	-0.674142000
7	8.163024000	-1.107790000	-2.530103000
6	7.210131000	-1.677776000	-3.496651000
1	7.431122000	-1.242985000	-4.492029000
6	9.559760000	-1.424091000	-2.932943000
1	10.184184000	-1.449687000	-2.018900000
1	9.641192000	-2.436850000	-3.387548000
6	10.080029000	-0.379666000	-3.922754000
7	10.003054000	0.991123000	-3.346917000

7	3.412823000	0.649856000	-0.913602000
6	2.279685000	-0.092213000	-1.531313000
6	2.114014000	0.311263000	-2.998331000
6	3.435506000	0.910444000	-4.998465000
6	3.804537000	2.370954000	-4.735709000
6	5.174391000	3.936186000	-3.527525000
7	6.427832000	4.168431000	-2.793195000
7	5.841734000	5.025905000	0.038130000
6	7.058573000	5.406559000	0.807650000
6	7.572982000	4.230229000	1.640124000
1	6.824026000	3.926360000	2.397048000
1	8.475426000	4.545806000	2.210111000
1	7.838222000	5.732491000	0.091252000
1	6.859899000	6.282835000	1.465305000
6	5.624528000	5.905070000	-1.142721000
1	4.561784000	5.813446000	-1.445503000
1	5.767582000	6.977212000	-0.872694000
6	6.534230000	5.573267000	-2.325734000
6	7.567537000	3.874199000	-3.679061000
6	8.642661000	2.200630000	-5.098749000
6	9.994158000	2.041859000	-4.401431000
6	11.131424000	1.203009000	-2.396269000
1	12.071965000	1.447057000	-2.939978000
1	11.323269000	0.248960000	-1.865269000
6	10.826726000	2.289992000	-1.376996000
1	10.728574000	3.278753000	-1.873365000
1	11.685202000	2.382415000	-0.673824000
1	10.291930000	2.999374000	-3.930569000
1	10.768294000	1.834094000	-5.175101000
1	8.386878000	1.267773000	-5.643960000
1	8.748180000	2.987625000	-5.885016000
1	7.581846000	4.597607000	-4.544747000
1	8.503235000	4.024259000	-3.105528000
1	7.595405000	5.743057000	-2.048142000
1	6.317330000	6.296997000	-3.148327000
6	4.652553000	5.043282000	0.936061000
6	3.532622000	4.151002000	0.424859000
7	4.025623000	2.772988000	0.175498000
6	2.958390000	1.961154000	-0.421814000
1	2.549764000	2.528165000	-1.282423000
1	3.124636000	4.537550000	-0.532027000
1	2.688102000	4.173858000	1.150617000
1	4.967881000	4.691614000	1.938149000
1	4.275369000	6.080751000	1.079045000
1	5.092128000	4.661534000	-4.387558000
1	4.314540000	4.120652000	-2.854685000
1	3.019451000	2.851748000	-4.115877000
1	3.795480000	2.915223000	-5.710641000
1	4.175108000	0.448996000	-5.683908000
1	2.464351000	0.882760000	-5.543858000
1	1.856954000	1.387002000	-3.064887000
1	1.259035000	-0.239822000	-3.451257000
1	2.486983000	-1.177104000	-1.439252000
1	1.323469000	0.082224000	-0.988341000
1	9.472386000	-0.401251000	-4.848106000

1	11.120682000	-0.628703000	-4.229877000
1	9.957506000	3.233142000	1.031664000
1	6.202706000	2.947919000	-5.806356000
1	6.208942000	1.236498000	-5.245530000
1	5.350376000	-1.256318000	-5.238473000
1	4.992159000	-2.859465000	-4.557940000
1	7.371091000	-2.781430000	-3.589660000
1	2.113625000	1.828312000	0.300599000
1	9.276376000	4.065018000	-0.393501000
1	5.527432000	-1.964747000	-2.380454000
1	7.979519000	-1.513775000	-1.601396000
1	7.770595000	2.195598000	1.329407000
1	4.272138000	2.355677000	1.087239000
1	3.777301000	0.104274000	-0.119625000
1	9.685699000	1.174129000	-0.088048000
8	6.452142000	1.246907000	-1.369009000

[**TREN**$_3$Cu^{II}Cu^{II}Cu^{II}(μ_3-O)] – BP86/def2-SVP (C, H, O, N)/def2-TZVP (Cu)

4, 4

29	4.991974000	0.732780000	-2.547108000
7	3.364416000	0.084940000	-3.778646000
6	3.494433000	-1.374536000	-4.087621000
1	3.085363000	-1.950454000	-3.234629000
1	2.869935000	-1.643707000	-4.968500000
6	4.939684000	-1.769071000	-4.323370000
7	5.790180000	-1.313320000	-3.185936000
7	5.093598000	2.496603000	-3.997332000
6	6.270367000	2.247922000	-4.858375000
7	7.541970000	2.472847000	-4.131124000
29	8.127298000	1.158401000	-2.355872000
29	6.168398000	3.068639000	-0.751028000
7	7.809573000	3.056339000	0.727388000
6	9.181456000	3.107412000	0.190815000
7	9.503235000	2.007546000	-0.730333000
7	8.158358000	-1.045940000	-2.527131000
6	7.193381000	-1.659967000	-3.457056000
1	7.436223000	-1.315951000	-4.481915000
6	9.552001000	-1.405002000	-2.937855000
1	10.182242000	-1.440966000	-2.028666000
1	9.599552000	-2.424449000	-3.378832000
6	10.076510000	-0.380949000	-3.940629000
7	10.009477000	0.995510000	-3.359258000
7	3.456886000	0.658138000	-0.959429000
6	2.294113000	-0.080299000	-1.546998000
6	2.106150000	0.327203000	-3.005934000
6	3.432161000	0.895147000	-5.031126000
6	3.812251000	2.347635000	-4.767722000
6	5.158135000	3.888854000	-3.494378000
7	6.406410000	4.147162000	-2.745325000
7	5.842040000	5.036448000	0.034923000
6	7.069103000	5.416226000	0.802160000
6	7.566075000	4.230080000	1.623558000
1	6.822838000	3.930018000	2.386920000
1	8.481690000	4.515101000	2.186201000
1	7.847884000	5.746420000	0.086556000

1	6.865153000	6.289859000	1.460130000
6	5.600324000	5.925512000	-1.139444000
1	4.532025000	5.839666000	-1.422757000
1	5.752081000	6.994164000	-0.863670000
6	6.495937000	5.587361000	-2.325577000
6	7.561578000	3.863118000	-3.629591000
6	8.671955000	2.227075000	-5.090859000
6	10.023304000	2.060775000	-4.404950000
6	11.135486000	1.187118000	-2.390486000
1	12.078290000	1.424421000	-2.931149000
1	11.315107000	0.226253000	-1.869107000
6	10.824376000	2.268200000	-1.372722000
1	10.777473000	3.269904000	-1.848200000
1	11.648455000	2.319192000	-0.626627000
1	10.337616000	3.009253000	-3.926520000
1	10.794590000	1.844729000	-5.178058000
1	8.414814000	1.310790000	-5.660913000
1	8.744287000	3.045514000	-5.843959000
1	7.552158000	4.577135000	-4.495465000
1	8.494454000	4.039840000	-3.061843000
1	7.558578000	5.782570000	-2.076057000
1	6.251243000	6.267679000	-3.173623000
6	4.656717000	5.040651000	0.950034000
6	3.546300000	4.147445000	0.432035000
7	4.077745000	2.785531000	0.136409000
6	2.999232000	1.946778000	-0.407843000
1	2.503092000	2.513329000	-1.221357000
1	3.108016000	4.549100000	-0.504640000
1	2.717611000	4.120496000	1.174515000
1	4.982692000	4.687040000	1.947242000
1	4.283502000	6.077770000	1.098287000
1	5.083376000	4.600381000	-4.358770000
1	4.287418000	4.069033000	-2.836476000
1	3.022627000	2.848546000	-4.171357000
1	3.858859000	2.895662000	-5.736520000
1	4.163500000	0.416862000	-5.713792000
1	2.457853000	0.867828000	-5.569238000
1	1.850174000	1.403217000	-3.076006000
1	1.253552000	-0.225191000	-3.459512000
1	2.489422000	-1.166851000	-1.452353000
1	1.357666000	0.106814000	-0.977096000
1	9.470191000	-0.400319000	-4.867268000
1	11.117317000	-0.628500000	-4.245072000
1	9.915816000	3.132291000	1.033007000
1	6.231795000	2.920808000	-5.755819000
1	6.250301000	1.204315000	-5.222756000
1	5.339786000	-1.305145000	-5.248854000
1	5.000579000	-2.869352000	-4.476467000
1	7.321063000	-2.769903000	-3.455305000
1	2.221383000	1.767054000	0.373925000
1	9.302692000	4.060302000	-0.362481000
1	5.494365000	-1.839555000	-2.346699000
1	7.986327000	-1.418029000	-1.580642000
1	7.706695000	2.193015000	1.281877000
1	4.373186000	2.368071000	1.034752000

1	3.850507000	0.092839000	-0.191869000
1	9.598273000	1.144987000	-0.168339000
8	6.450609000	1.284085000	-1.417582000

[**TREN**$_4$Cu^{I}Cu^{I}Cu^{II}(μ_3-OH)] – TPSSh/def2- TZVP (TD-DFT)

3, 2

29	9.863709000	-0.255723000	10.292554000
6	10.996198000	1.975354000	12.070077000
1	11.009247000	2.886877000	12.700143000
1	12.011053000	1.879665000	11.655274000
6	8.394522000	-1.357951000	12.903464000
1	7.912575000	-2.129739000	13.534778000
1	8.092595000	-0.389376000	13.329232000
7	7.892816000	-1.394897000	11.512450000
6	9.905498000	-1.535335000	13.002691000
1	10.196914000	-1.512594000	14.068425000
1	10.188046000	-2.529058000	12.628443000
7	10.678965000	-0.518770000	12.233431000
7	11.664062000	-1.539717000	9.645162000
7	12.065839000	-0.142993000	7.738207000
7	10.868347000	-2.238593000	7.454234000
6	10.681852000	0.782202000	12.966313000
1	11.415535000	0.755193000	13.792111000
1	9.700541000	0.909767000	13.440207000
6	11.427041000	-2.684149000	8.746803000
1	10.721391000	-3.370771000	9.232890000
1	12.383882000	-3.230268000	8.573150000
6	7.869488000	-2.766267000	10.993029000
1	7.216418000	-3.409952000	11.633127000
1	8.883266000	-3.188673000	11.014811000
6	12.082067000	-0.995383000	12.046313000
1	12.475399000	-1.422054000	12.986130000
1	12.708463000	-0.122883000	11.817099000
6	11.802554000	-1.255963000	6.841092000
1	11.341095000	-0.880102000	5.920946000
1	12.749456000	-1.783781000	6.563662000
6	12.638072000	-0.643691000	8.975244000
1	12.868770000	0.204208000	9.632619000
1	13.587265000	-1.211572000	8.803081000
6	12.363314000	1.645696000	5.957453000
1	12.087599000	0.954393000	5.150228000
1	13.178325000	2.273903000	5.537934000
6	12.204642000	-2.034433000	10.937301000
1	13.263140000	-2.338398000	10.844876000
1	11.645727000	-2.944036000	11.203832000
6	12.966250000	0.856304000	7.122064000
1	13.266756000	1.545121000	7.925146000
1	13.902905000	0.384603000	6.759948000
29	8.702366000	-1.652336000	7.771688000
6	10.739917000	-3.388253000	6.516339000
1	11.649199000	-4.017716000	6.522337000
1	10.668836000	-2.964932000	5.503717000
6	7.394857000	-4.168657000	9.101675000
1	6.604674000	-4.779748000	9.579532000
1	8.352281000	-4.618290000	9.405667000

7	7.388331000	-2.776360000	9.604639000
6	7.218453000	-4.253454000	7.590769000
1	7.220178000	-5.315876000	7.287668000
1	6.235404000	-3.853949000	7.310064000
7	8.252059000	-3.494233000	6.832302000
7	7.214861000	-0.850763000	5.830471000
7	8.609598000	1.040664000	5.406815000
7	6.541636000	1.340543000	6.642776000
6	9.529505000	-4.267559000	6.806790000
1	9.481000000	-5.071846000	6.050631000
1	9.646750000	-4.768952000	7.776325000
6	6.082530000	0.039031000	6.102565000
1	5.428087000	-0.446095000	6.840381000
1	5.487319000	0.217436000	5.173478000
6	6.024859000	-2.225177000	9.583361000
1	5.342101000	-2.879762000	10.181194000
1	5.651344000	-2.206024000	8.550520000
6	7.774170000	-3.256183000	5.436355000
1	7.355140000	-4.187551000	5.015129000
1	8.648212000	-3.005856000	4.820058000
6	7.504236000	1.941928000	5.681483000
1	7.888163000	2.869412000	6.122072000
1	6.956656000	2.207012000	4.741098000
6	8.089357000	-0.193984000	4.843498000
1	8.930023000	-0.856679000	4.598821000
1	7.514700000	-0.012626000	3.897536000
6	10.407617000	2.797693000	5.103654000
1	9.729009000	3.619106000	5.368236000
1	11.056322000	3.203153000	4.297868000
6	6.726711000	-2.150674000	5.329262000
1	6.395559000	-2.088928000	4.274503000
1	5.829874000	-2.419329000	5.908369000
6	9.601100000	1.648027000	4.497327000
1	10.276769000	0.838359000	4.183313000
1	9.126301000	2.022479000	3.566691000
29	7.158111000	1.128257000	8.846880000
8	8.851378000	0.136057000	8.622385000
6	5.387653000	2.271853000	6.762782000
1	4.771943000	2.267856000	5.843496000
1	5.801486000	3.287524000	6.849266000
6	4.613268000	-0.354338000	10.070969000
1	3.984521000	-0.847535000	10.838310000
1	4.188648000	-0.648092000	9.098945000
7	6.006374000	-0.852643000	10.104899000
6	4.505395000	1.153132000	10.265351000
1	3.437766000	1.437399000	10.267220000
1	4.899720000	1.428169000	11.252638000
7	5.248070000	1.941203000	9.241585000
7	7.869196000	2.897880000	10.228261000
7	9.777036000	3.353388000	8.859463000
7	10.074835000	2.120060000	10.919291000
6	4.490892000	1.963103000	7.955470000
1	3.675900000	2.707542000	7.998122000
1	4.005410000	0.987623000	7.826170000
6	8.767107000	2.621324000	11.368701000

1	8.286735000	1.864398000	12.004481000
1	8.899749000	3.552346000	11.972786000
6	6.524587000	-0.862005000	11.479286000
1	5.855095000	-1.468687000	12.139473000
1	6.541944000	0.163571000	11.872634000
7	11.178739000	2.441302000	6.302162000
6	5.459492000	3.336250000	9.732359000
1	4.530342000	3.733246000	10.178285000
1	5.682589000	3.969852000	8.863544000
6	10.672572000	3.089564000	9.975105000
1	11.608257000	2.660712000	9.597428000
1	10.924299000	4.037686000	10.517402000
6	8.535482000	3.903527000	9.367139000
1	7.879577000	4.155901000	8.523339000
1	8.698406000	4.837310000	9.964318000
6	11.542249000	3.638522000	7.071755000
1	12.354632000	3.369975000	7.759526000
1	11.960118000	4.438051000	6.423372000
6	6.586956000	3.429677000	10.753219000
1	6.688198000	4.480456000	11.081520000
1	6.330941000	2.853114000	11.655149000
6	10.388442000	4.256563000	7.865101000
1	9.584375000	4.565586000	7.180776000
1	10.761834000	5.189483000	8.335733000
1	9.434888000	0.686981000	8.049087000

[**TREN₄**$Cu^{I}Cu^{II}Cu^{II}$(μ_3-OH)] – TPSSh/def2- TZVP (TD-DFT)

4, 3

29	11.335532000	5.561258000	4.697933000
29	8.965119000	7.918370000	4.633196000
29	10.784921000	7.414099000	7.401208000
8	10.730231000	7.342440000	5.391752000
7	9.601658000	4.305787000	5.913186000
7	7.029813000	8.308150000	3.899175000
7	13.401160000	5.559503000	5.643785000
7	9.568134000	7.902492000	2.447341000
7	8.587901000	9.829380000	5.860954000
7	13.898996000	7.892185000	6.169954000
7	10.817242000	10.653486000	5.504129000
7	11.824082000	3.613733000	4.072882000
7	8.827917000	5.861894000	7.608814000
7	12.843888000	6.511488000	7.830235000
7	12.003851000	8.060406000	2.439214000
7	10.259138000	9.604626000	7.637565000
7	7.809035000	5.863488000	5.401357000
7	10.593006000	7.343613000	9.503238000
7	13.484446000	10.128058000	4.116902000
7	10.964562000	5.887885000	2.440322000
6	8.832687000	9.837002000	7.319098000
6	14.318335000	6.717565000	5.422672000
6	13.302045000	5.311117000	7.100235000
6	13.849898000	7.579865000	7.586690000
6	9.703921000	6.505471000	1.974771000
6	10.762776000	8.676379000	1.997320000
6	6.025334000	7.408828000	4.542013000

6	8.337969000	4.504391000	5.181463000
6	12.085941000	6.710405000	1.912499000
6	7.577771000	6.036620000	6.846988000
6	9.335141000	4.505255000	7.350433000
6	8.505515000	6.025135000	9.054182000
6	12.080056000	3.659203000	2.600672000
6	13.183638000	8.840751000	1.981640000
6	11.082829000	10.633492000	6.933827000
6	9.409891000	10.922269000	5.275417000
6	9.738224000	6.194726000	9.926836000
6	14.798067000	9.626855000	4.537536000
6	11.045542000	4.507373000	1.875074000
6	7.137558000	10.102151000	5.628197000
6	14.026838000	4.371006000	4.977902000
6	10.082301000	2.906945000	5.732732000
6	8.372672000	8.539775000	1.806574000
6	6.712916000	9.735270000	4.213219000
6	10.708835000	2.665513000	4.368416000
6	13.058429000	3.210634000	4.812072000
6	14.821937000	9.034936000	5.946933000
6	9.985465000	8.636213000	9.944026000
6	13.356230000	10.198859000	2.657310000
6	10.481005000	9.803457000	9.106326000
6	12.792143000	6.181799000	9.287073000
6	11.635329000	11.684212000	4.816715000
6	11.969865000	7.196163000	10.067759000
6	6.517466000	5.974820000	4.664162000
6	13.136111000	11.396799000	4.766973000
6	7.058219000	8.087045000	2.421944000
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1	15.351169000	6.402646000	5.708833000
1	14.315674000	6.947249000	4.350434000
1	12.596182000	4.490998000	7.285384000
1	14.297583000	5.003360000	7.490710000
1	14.835861000	7.234382000	7.982888000
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1	8.860627000	5.910864000	2.350337000
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1	10.727366000	8.757807000	0.883665000
1	10.685612000	9.688059000	2.412661000
1	5.787257000	7.817501000	5.531771000
1	5.082215000	7.418837000	3.968611000
1	8.511656000	4.363880000	4.107223000
1	7.588524000	3.745599000	5.508546000
1	12.043824000	6.687767000	0.796576000
1	13.041290000	6.265379000	2.220610000
1	6.809579000	5.306759000	7.197120000
1	7.193915000	7.047363000	7.038135000
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1	10.271630000	4.350479000	7.900881000
1	7.850100000	6.903510000	9.140753000
1	7.918495000	5.168319000	9.435427000
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1	12.084114000	2.640194000	2.176174000

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1	10.872417000	11.626756000	7.399653000
1	9.228673000	10.980199000	4.194583000
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1	10.352229000	5.285700000	9.904579000
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1	15.573156000	10.420366000	4.509497000
1	10.046680000	4.052990000	1.951180000
1	11.288508000	4.532363000	0.798059000
1	6.568520000	9.518445000	6.366143000
1	6.894262000	11.162363000	5.817872000
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1	5.633189000	9.927657000	4.091020000
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1	14.233613000	10.689342000	2.186552000
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1	5.726963000	5.368833000	5.144445000
1	13.550766000	11.393785000	5.784266000
1	13.612618000	12.264046000	4.265301000
1	6.893461000	7.018939000	2.230208000
1	6.223248000	8.618437000	1.933931000
1	11.389742000	8.002306000	5.060312000

8. Reference

(1) Yakelis, N. A.; Bergman, R. G. Safe Preparation and Purification of Sodium Tetrakis[(3,5-Trifluoromethyl) Phenyl]Borate ($NaBArF_{24}$): Reliable and Sensitive Analysis of Water in Solutions of Fluorinated Tetraarylborates. *Organometallics* **2005**, *24*, 3579.

(2) Stoll, S.; Schweiger, A. EasySpin, a Comprehensive Software Package for Spectral Simulation and Analysis in EPR. *J. Magn. Reson.* **2006**, *178*, 42.
(3) Sequoia, E.; Laboratoire, O. N.; Organique, P.; Gabriel, S. General Expression of the linear Potential Sweep voltammogram in the Case of diffusionless Electrochemical Systems. **1979**, *101*, 19.
(4) Sivasankaran, U.; Vikraman, A. E.; Thomas, D. Nanomolar Level Determination of Octyl Gallate in Fats and Oils. *Food Anal. Methods* **2016**, 2115.
(5) Nicholson, R. S. Theory and Application of Cyclic Voltammetry for Measurement of Electrode Reaction Kinetics. *Anal. Chem.* **1965**, *37*, 1351.
(6) Lavagnini, I.; Antiochia, R.; Magno, F. An Extended Method for the Practical Evaluation of the Standard Rate Constant from Cyclic Voltammetric Data. *Electroanalysis* **2004**, *16*, 505.
(7) Gennari, M.; Pøcaut, J.; Debeer, S.; Neese, F.; Collomb, M.; Duboc, C. A Fully Delocalized Mixed-Valence Bis-μ-(Thiolato) Dicopper. *Angew. Chem. Int. Ed.* **2011**, *50*, 5662.
(8) Weaver, M. J. An Alternative Approach to the Intercomparison of Electron-Transfer Reactivities at Metal Surfaces and in Homogeneous Solution1. *J. Phys. Chem.* **1990**, *94*, 8608.
(9) Neese, F. Software Update : The ORCA Program System, Version 4.0. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8*, 4.
(10) Viktor N. Staroverov and Gustavo E. Scuseria. Comparative Assessment of a New Nonempirical Density Functional : Molecules and Hydrogen-Bonded Complexes. *J. Chem. Phys.* **2004**, *119*, 12129.
(11) Marenich, A. V; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378.
(12) Johnson, E. R.; Becke, A. D. A Post-Hartree-Fock Model of Intermolecular Interactions: Inclusion of Higher-Order Corrections. *J. Chem. Phys.* **2006**, *124*, 174104.
(13) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456.
(14) Koepke, S. J.; Light, K. M.; Vannatta, P. E.; Wiley, K. M.; Kieber-Emmons, M. T. Electrocatalytic Water Oxidation by a Homogeneous Copper Catalyst Disfavors Single-Site Mechanisms. *J. Am. Chem. Soc.* **2017**, *139*, 8586.