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SUPPORTING INFORMATION

Influence of Intramolecular Secondary Sphere Hydrogen-Bonding Interactions on Cytochrome *c* Oxidase Inspired Low-Spin Heme-Peroxo-Copper Complexes

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I. Materials and Methods

General: All reagents and solvents purchased and used were of commercially available quality except as noted. MeTHF and THF were distilled over Na/benzophenone under Ar. The complexes, $[Cu^{I}(CH_3CN)_4(BAr^F)]$, $(F_8)Fe^{II}$ and d_8-F_8Fe^{II} were synthesized as previously described.[1,2] Preparation and handling of air sensitive complexes were performed in a Vac atmosphere OMNI-LAB drybox or under argon atmosphere using standard Schlenk techniques. Solvent deoxygenation was achieved by bubbling Ar through the desired solvent for ≥ 45 minutes via an addition funnel connected to a receiving Schlenk flask. UV-vis measurements were carried out by using a Carey-50 Bio spectrophotometer with a 10 mm path quartz cell. The spectrometer was equipped with Cary WinUV Scanning Kinetics software and a Unisoku thermostat cell holder for low temperature experiments. All ^1H, ^2H, and ^{13}C NMR spectra were recorded in 9 inch, 5 mm o.d. NMR tubes on a 300 MHz Bruker AVANCE NMR instrument, wherein ^2H NMR collection utilized a BBFO probe with the X channel tuned to 46.072Mhz for enhanced deuterium detection. The ^2H chemical shifts were calibrated with respect to the residual deuterium solvent peaks. ^1H and ^{13}C NMR chemical shift values were also assigned relative to residual solvent. Resonance Raman samples were excited at a variety of wavelengths (413 nm excitation unless otherwise noted with data), using either a Coherent I90C-K Kr^+ ion laser, a Coherent 25/7 Sabre Ar^+ ion laser, or an Ar^+ pumped Coherent Ti:Saph laser while the sample was immersed in a liquid nitrogen cooled (77 K) EPR finger dewar (Wilmad). Power was ~2 mW at the sample for the high-energy lines and >200 mW at the low energy lines. Data were recorded while rotating the sample to minimize photodecomposition. The spectra were recorded using a Spex 1877 CP triple

monochromator with either a 600, 1200, or 2400 groves/mm holographic spectrograph grating, and detected by an Andor Newton CCD cooled to –80 °C (for high energy excitation) or an Andor IDus CCD cooled to –80 °C (for the low energy excitation). Spectra were calibrated on the energy axis to toluene. Excitation profiles were intensity calibrated to the solvent (MeTHF) by peak fitting in the program Origin. EPR spectra were collected on an X-band Bruker EMX EPR spectrometer: microwave frequency = 9.42 GHz, microwave power = 0.201 mW, attenuation = 30 db, modulation amplitude = 10 G, modulation frequency = 100 kHz, temperature = 10 K. Electrochemical experiments were performed using a BAS 100B electrochemical analyzer. Infrared spectra of copper complexes were collected in CH_3CN on a ThermoNicolet Nexus 670 FTIR spectrometer using Specac solution IR cell fit with CaF_2 windows. Infrared spectra of organic compounds were also collected on a ThermoNicolet Nexus 670 FTIR spectrometer using neat compounds via attenuated total reflectance (ATR) FTIR. Mass spectra for organic compounds were collected on a VG Analytical VG-70S Magnetic Sector Mass Spectrometer using electron impact (EI) ionization. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, DE. and Midwest Microlab, Indianapolis, IN.

II. Synthesis of ligands and copper-ligand complexes $[(^{X}TMPA)Cu^{I}]BAr^{F}$ and $[(^{X}TMPA)Cu^{II}(N_3^-)]ClO_4$:

The ligands and Cu(I) complexes, ^{X}TMPA (X = -H, $-CH_3$, $(-CH_3)_2$, $-NH_2$, $(-NH_2)_2$, PV), $[(TMPA)Cu^{I}(CH_3CN)]BAr^{F}$, and $[(^{PV}TMPA)Cu^{I}]BAr^{F}$ have been synthesized from published procedures.[3–8] The Cu(II)-azido complexes, $[(TMPA)Cu^{II}(N_3^-)]ClO_4$,

[(^{NH2}TMPA)$Cu^{II}(N_3^-)$]ClO_4, [($^{(NH2)2}$TMPA)$Cu^{II}(N_3^-)$]ClO_4, [(^{CH3}TMPA)$Cu^{II}(N_3^-)$]ClO_4, and [(^{PV}TMPA)$Cu^{II}(N_3^-)$]ClO_4 were also synthesized from published procedures.[5,6]

^{NH2,CH3}TMPA:

The ligand ^{NH2,CH3}TMPA was synthesized per Figure S1.

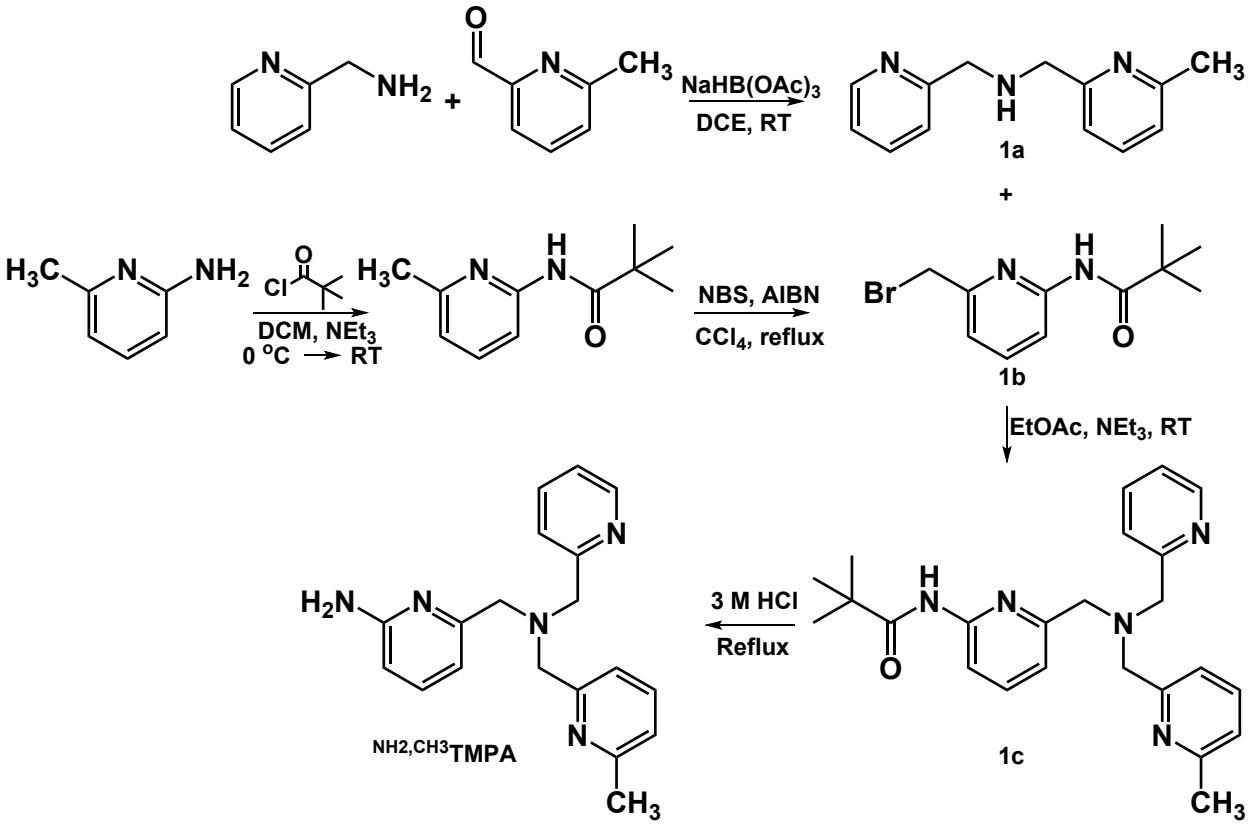


Figure S1. Synthetic route for the ligand ^{NH2,CH3}TMPA.

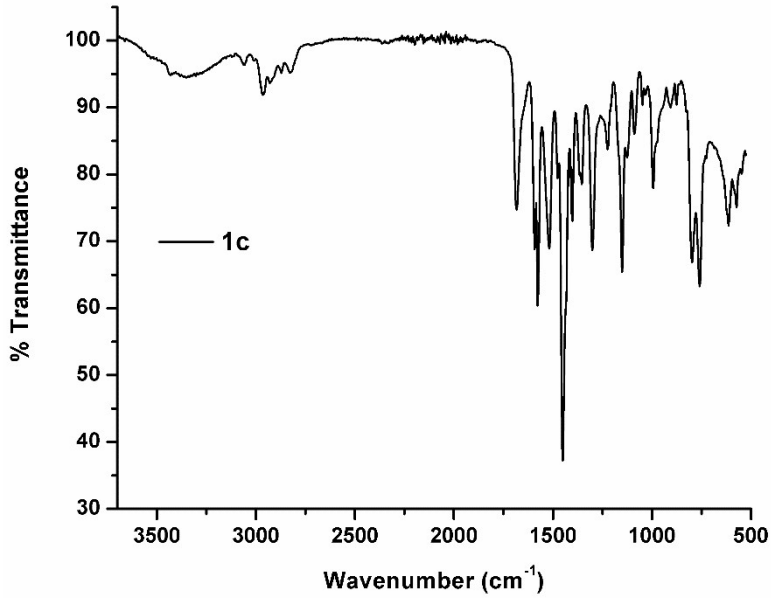
N-(2-pyridylmethyl)-*N*-(6-methyl-2-pyridylmethyl)amine (**1a**): *N*-(2-pyridylmethyl)-*N*-(6-methyl-2-pyridylmethyl)amine was synthesized by a modified literature procedure.[9] 2-pyridylmethylamine (1.61 g, 14.89 mmol, 1.2 equiv.) and 6-methyl-2-

pyridinecarboxaldehyde (1.50 g, 12.38 mmol, 1.0 equiv.) were added to a 250-mL round-bottom flask and dissolved in dichloroethane (80 mL). After 10 minutes of stirring, $NaBH(OAc)_3$ (3.95 g, 18.64 mmol, 1.5 equiv.) was added to the flask and the reaction was stirred under Ar at room temperature for 19 hours. Water (50 mL) was added to the flask, followed by acidification (until pH 2) via dropwise addition of concentrated HCl. The aqueous layer was extracted with dichloromethane (3 x 100 mL), then basified (until pH 9) via addition of a concentrated aqueous solution of K_2CO_3. The aqueous layer was extracted with dichloromethane (3 x 100 mL), the organic fractions were combined, dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo* to give a yellow oil (3.909 g, 95%). ^{1}H-NMR ($CDCl_3$): 8.55 (ddd, 0.84 Hz, 1.76 Hz, 4.86 Hz, 1H), 7.64 (dt, 1.84 Hz, 7.64 Hz, 1H), 7.53 (t, 7.68 Hz, 1H), 7.36 (d, 7.76 Hz, 1H), 7.16 (m, 1H), 7.01 (dd, 0.44 Hz, 7.67 Hz, 1H), 3.99 (s, 2 H), 3.95 (s, 2H), 2.53 (s, 3H).

N-(6-methyl-2-pyridylmethyl)-*N*-(6-pivalamido-2-pyridylmethyl)-*N*-(2-pyridylmethyl)amine (**1c**): *N*-(2-pyridylmethyl)-*N*-(6-methyl-2-pyridylmethyl)amine (**1a**) (1.9177 g, 8.99 mmol, 1 equiv.) and 2-(bromomethyl)-6-(pivalamido)pyridine (**1b**)[8] (3.66 g, 13.50 mmol, 1.5 equiv.) were added to a 250-mL round-bottom flask, then dissolved in 150 mL of ethyl acetate. Triethylamine (2.34 g, 23.12 mmol, 2.6 equiv.) was added and the reaction was stirred at room temperature for 9 hours. After removal of solvent, a saturated aqueous solution of K_2CO_3 (100 mL) was added to the flask and then extracted with dichloromethane (3 x 100 mL). Removal of solvent *in vacuo* resulted in a brown oil, which was purified on an alumina column with varying eluating solvents (100% hexanes; hexanes:ethyl acetate 3:1; ethyl acetate:methanol 95:5) to give 2.1928 g (60.4%) of a

brown oil (R_f (alumina, ethyl acetate:methanol 95:5) = 0.84). ^{1}H-NMR ($CDCl_3$): 8.51 (ddd, 0.76 Hz, 1.6 Hz, 4.93 Hz 1H), 8.07 (m, 1H), 8.03 (s, 1H), 7.64 (m, 1H), 7.54 (m, 1H), 7.41 (d, 7.64 Hz, 1H), 6.99 (d, 7.52 Hz, 1H), 3.87 (s, 2H), 3.84 (s, 2H), 3.78 (s, 2H), 2.51 (s, 3 H), 1.31 (s, 9 H). ^{13}C-NMR ($CDCl_3$): 177.1, 159.4, 158.6, 157.7, 157.6, 150.9, 149.0, 138.7, 136.7, 136.4, 122.9, 122.0, 121.5, 119.7, 118.6, 112.0, 60.4, 60.2, 59.8, 39.8, 27.5, 24.4. EI-MS: 403.2 (M^+).

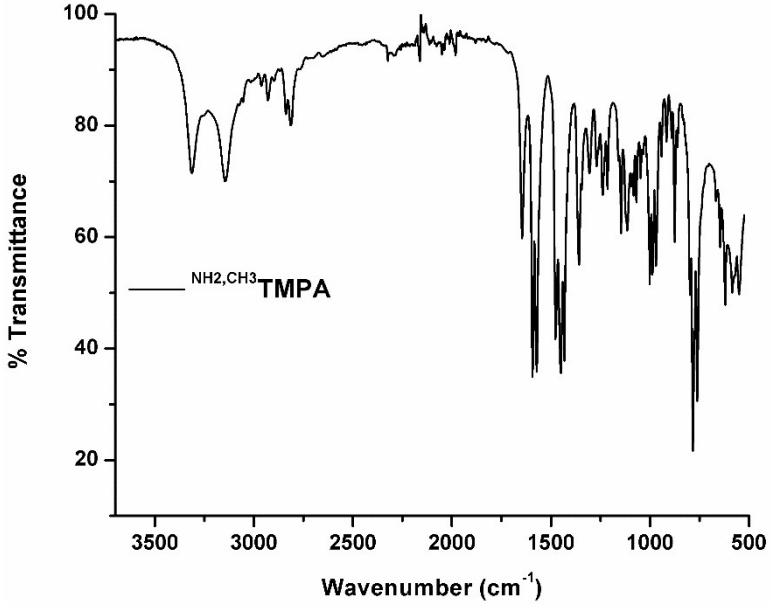
IR (neat, ATR): C=O stretch 1684 cm^{-1},

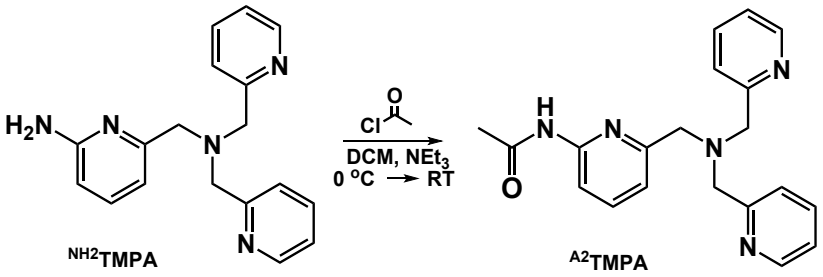


^{NH2,CH3}TMPA: *N*-(6-methyl-2-pyridylmethyl)-*N*-(6-pivalamido-2-pyridylmethyl)-*N*-(2-pyridylmethyl)amine (0.9114 g, 2.26 mmol) was dissolved in 3 M HCl (75 mL) and added to a 100-mL round-bottom flask. The solution was refluxed for 14 hours, cooled to room temperature, then basified (until pH 8) via dropwise addition of a saturated aqueous solution of K_2CO_3. The aqueous layer was extracted with dichloromethane (3 x 100 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was removed *in*

vacuo resulting in a yellow oil which was further purified with an alumina column using Ethyl acetate:Ethanol 9:1 as eluent. Removal of solvent resulted in a brown solid which was further purified by recrystallization from hot petroleum ether to give 0.5 g (69.3%) of a tan solid (R_f (alumina, ethyl acetate:ethanol 9:1) = 0.54). ^{1}H-NMR ($CDCl_3$): 8.50 (m, 1H), 7.63 (m, 1H), 7.53 (t, 7.64 Hz, 1H), 7.41 (m, 2H), 7.11 (m, 1H), 6.98 (d, 7.48 Hz, 1H), 6.95 (d, 7.36 Hz, 1H), 6.35 (d, 8.08 Hz, 1H), 4.41 (s, 2H (NH_2)), 3.87 (s, 2H), 3.85 (s, 2H), 3.70 (s, 2H), 2.51 (s, 3H). ^{13}C-NMR ($CDCl_3$): 159.8, 159.0, 158.0, 157.9, 157.5, 149.0, 138.1, 136.7, 136.4, 122.7, 121.9, 121.4, 119.5, 112.5, 106.7, 60.3, 60.2, 60.0, 24.4. EI-MS: 319.2 (M^+).

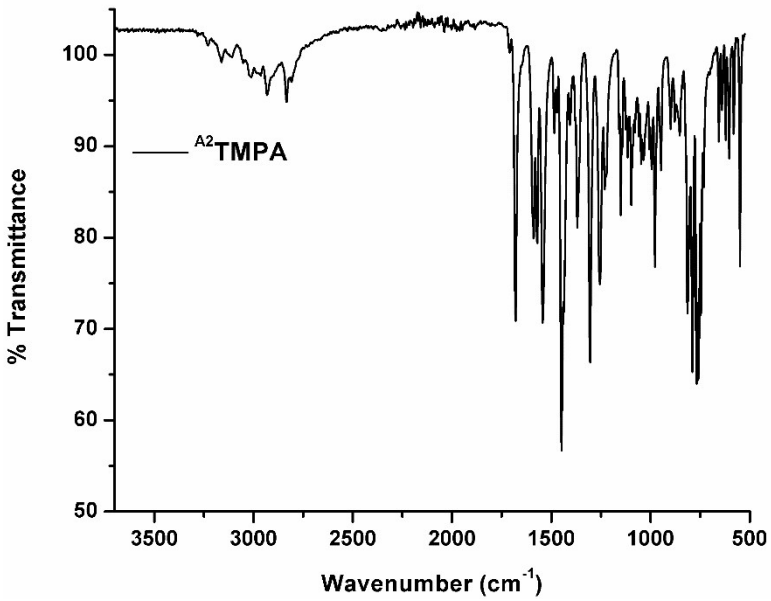
IR (neat, ATR): N–H stretches 3314 and 3145 cm^{-1}.

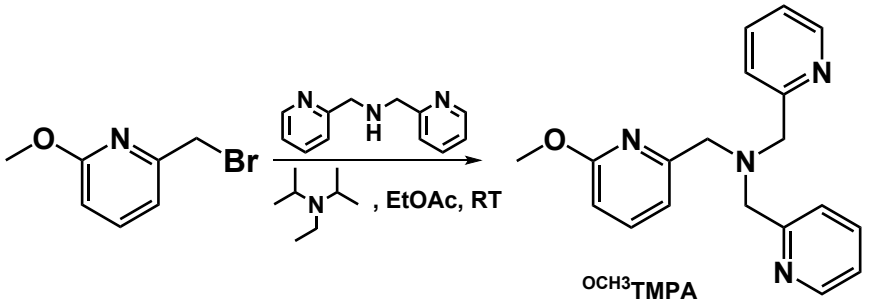




^{A2}TMPA: ^{NH2}TMPA (0.2712g, 0.89 mmol) was dissolved in dichloromethane (10 ml) and added to a 25-mL round-bottom flask. The round bottom was subjected to ten quick vacuum/Ar purges and triethylamine (130 ul, 0.932 mmol) was added to the solution. The reaction mixture was cooled to 0 ^{o}C in an ice-water bath and stirred for 30 minutes under argon. Acetyl chloride (63 ul, 0.89 mmol) was added dropwise to the reaction, which was then stirred at 0 ^{o}C for two hours. The reaction was then warmed to room temperature and stirred for an additional two hours. The reaction mixture was filtered to remove precipitate and the solid was washed with hexanes. The filtrate was concentrated to give an off-white solid (R_f (alumina, ethyl acetate:methanol 95:5) = 0.61). ^{1}H-NMR ($CDCl_3$): 8.53 (ddd, 4.86 Hz, 0.96 Hz, 0.92 Hz, 2H), 8.03 (d, 8.12 Hz, 1H), 7.66 (td, 7.7 Hz, 1.8 Hz, 4H), 7.56 (d, 7.8 Hz, 2H), 7.26 (d, 7.5 Hz, 1H), 7.15 (m, 2H), 3.89 (s, 4H), 3.77 (s, 2H), 2.19 (s, 3H). ^{13}C-NMR ($CDCl_3$): 168.6, 159.3, 157.6, 150.6, 149.1, 138.8, 136.5, 122.9, 122.1, 118.9, 111.9, 60.1, 59.7, 24.8. EI-MS: 347.2 (M^+).

IR (neat, ATR): amide C=O stretch at 1680 cm^{-1}.

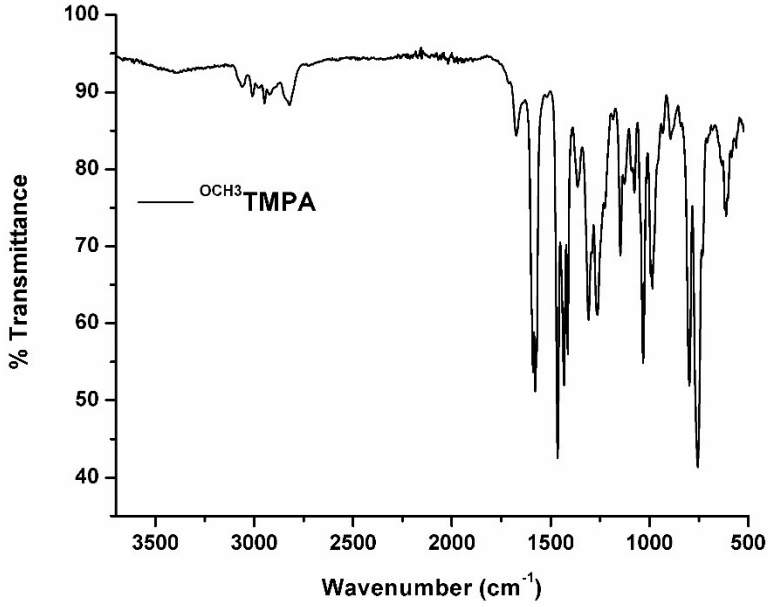




^{OCH3}TMPA: 2-bromo-6-methoxypyridine[10] (8.28 g, 40.98 mmol, 1.65 equiv.), di-(2-picolyl)amine (4.950 g, 24.84 mmol, 1 equiv.), and *N*,*N*-diisopropylethylamine (9.55 g, 73.89 mmol, 2.97 equiv.) were added to a 500-mL round-bottom flask, followed by 250 mL of ethyl acetate. The round bottom was subjected to five quick vacuum/Ar purges and the reaction was stirred under Ar overnight. The dark brown reaction mixture was concentrated to give a brown oil, which was washed with aqueous potassium carbonate and extracted with dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, and concentrated to give a brown oil. This crude product was

purified via a SiO_2 column using a solvent gradient starting with 1:1 hexanes:EtOAc, gradually increasing polarity to EtOAc, and then further increasing polarity to 4:1 EtOAc:MeOH. The product was obtained as a dark red oil (R_f (silica, 4:1 EtOAc:MeOH) = 0.51). ^{1}H-NMR ($CDCl_3$): 8.52 (dt, 4.8 Hz, 1.4 Hz, 2H), 7.66-7.63 (m, 4H), 7.51 (dd, 7.3 Hz, 0.96 Hz, 1H), 7.15-7.10 (m, 2H), 7.05 (dd, 7.2 Hz, 0.64 Hz, 1H), 6.58 (dd, 8.4 Hz, 0.68 Hz, 1H), 3.92 (s, 6H), 3.78 (s, 3H). ^{13}C-NMR ($CDCl_3$): 163.7, 159.8, 156.9, 149.1, 138.8, 136.5, 122.8, 122.0, 115.5, 108.8, 60.2, 59.6, 53.3. EI-MS: 320.2 (M^+).

IR (neat, ATR):



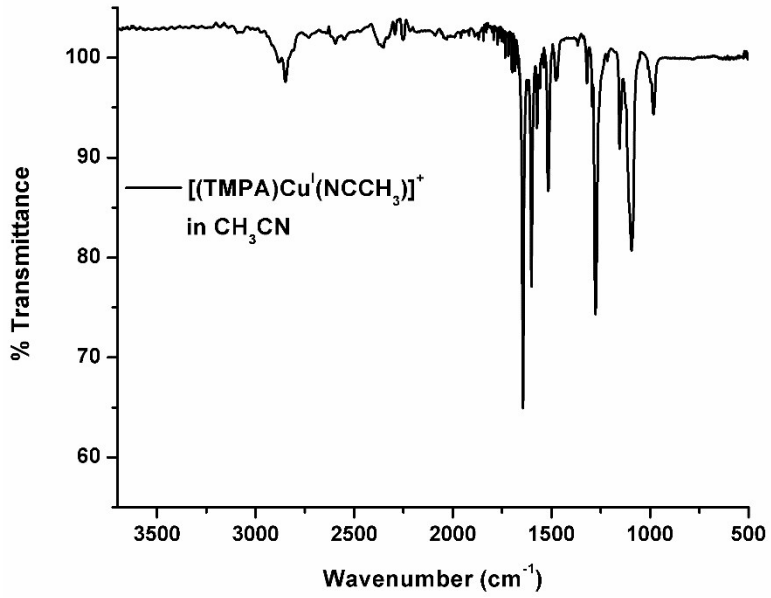
[(^{X}TMPA)Cu^I]BAr^F complexes:

In an inert atmosphere glovebox, the ligand (typically 35-50 mg, 0.11-0.16 mmol) was dissolved in 2 mL of THF in a 20 mL scintillation vial equipped with a stir bar. An equimolar amount of solid [Cu^I($CH_3CN)_4$]BArF was added to the stirring ligand solution. After stirring for 10 minutes, 18 mL of pentane was added to the solution, resulting in the formation of

a precipitate. Following decanting of the supernatant, the solid was dried and then re-dissolved in ~2 mL of THF and passed through a plug of celite. To the resulting solution was added ~18 mL of pentane to give a precipitate, which was then dried to give a free-flowing powder.

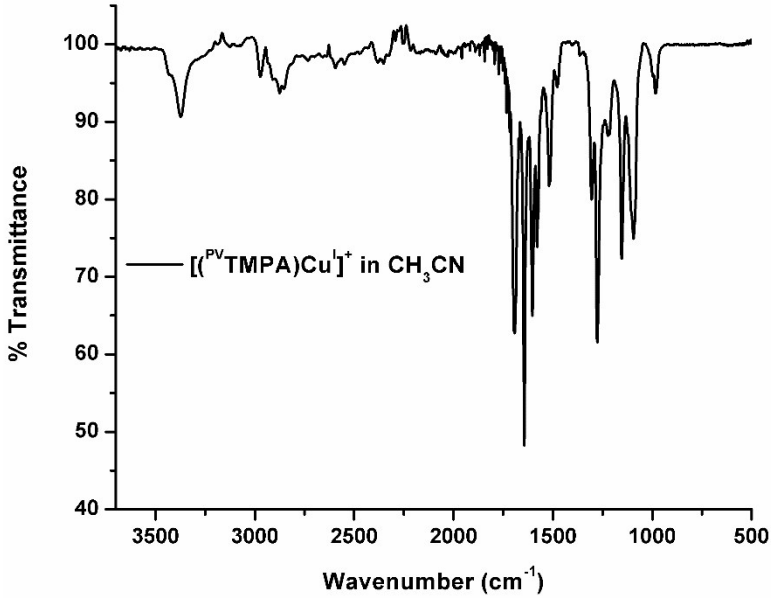
[(TMPA)Cu^{I}(NCCH$_3$)]BAr^{F}

IR (CH_3CN):



[(^{PV}TMPA)Cu^{I}]BAr^{F}

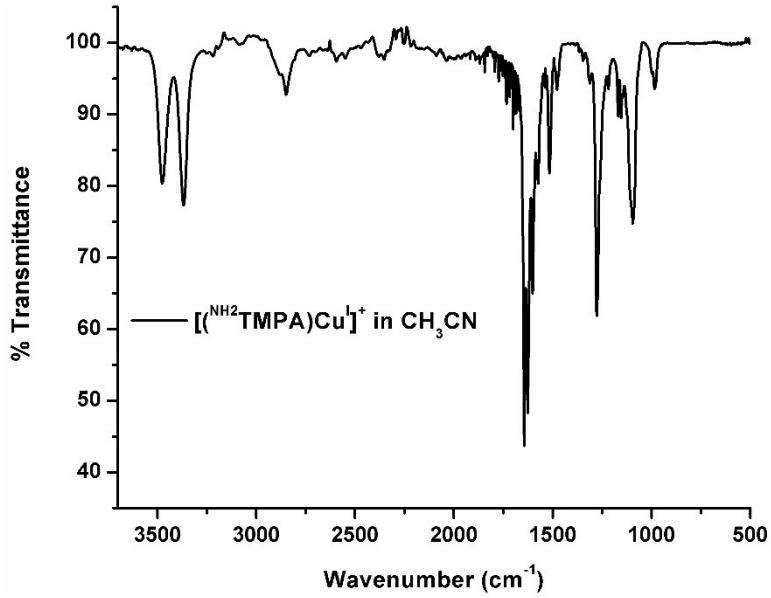
IR (CH_3CN): N–H stretch 3373 cm^{-1}; amide carbonyl stretch, 1696 cm^{-1}.



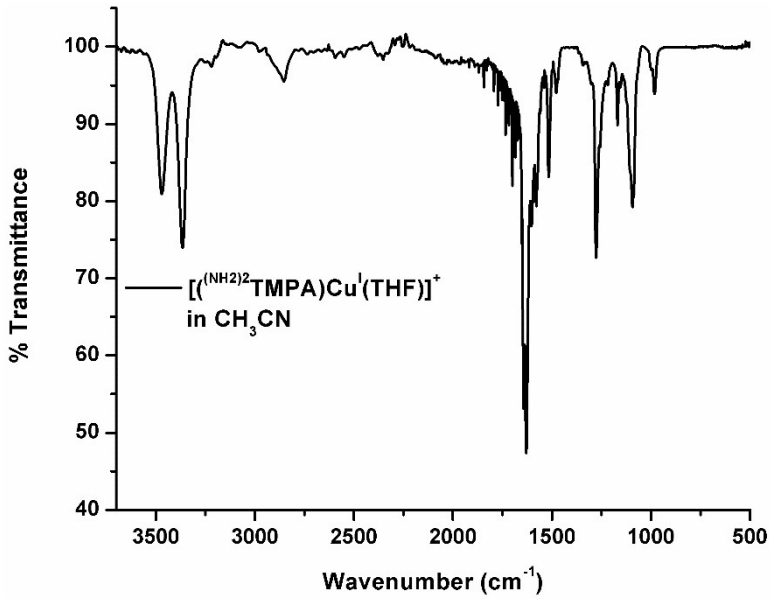
[(^{NH2}TMPA)Cu^{I}]BAr^{F}: ^{1}H-NMR (DMSO-d_6): 8.66 (d, 4.16 Hz, 2H), 7.79 (t, 7.48 Hz, 2H), 7.39 (m, 5H), 6.72 (d, 4.12 Hz, 2H), 6.47 (d, 7.72 Hz, 2H), 4.06 (s, 4H), 3.85 (s, 2H).

Calcd for $C_{42}H_{19}N_5BCuF_{20}$: C, 48.14; H, 1.83; N, 6.68. Found: C, 47.99; H, 2.09; N, 6.48.

IR (CH_3CN): N–H stretches 3475 and 3367 cm^{-1}.



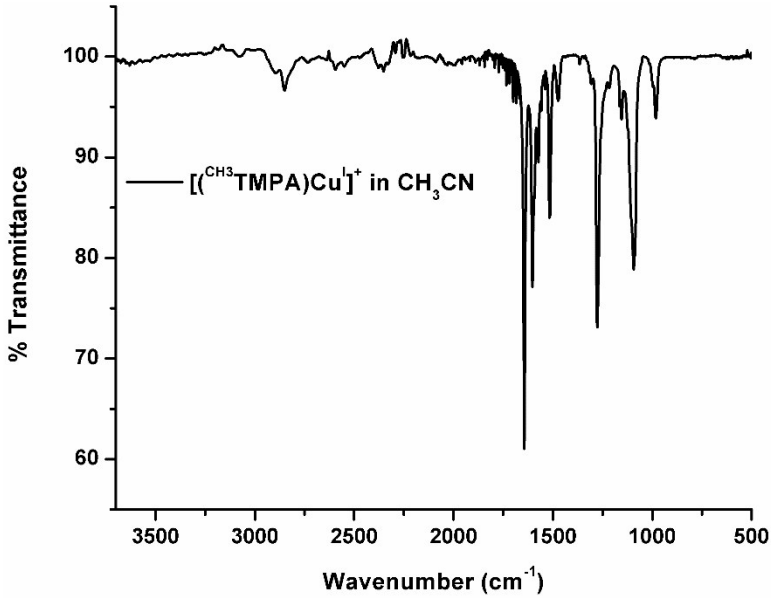
[($^{(NH2)2}$TMPA)Cu^{I}(THF)]BAr^{F}: ^{1}H-NMR (DMSO-d_6): 8.74 (d, 4.96 Hz, 1H), 7.83 (t, 7.6 Hz, 1H), 7.41 (m, 4H), 6.81 (s, 4H), 6.49 (dd, 4.08 Hz, 8.24 Hz, 4H), 4.02 (s, 2H), 3.82 (4H). Calcd for $C_{46}H_{28}N_6BCuF_{20}O$: C, 48.67; H, 2.49; N, 7.40. Found: C, 48.45; H, 2.67; N, 7.11. IR (CH_3CN): N–H stretches 3470 and 3365 cm^{-1}.



[(^{CH3}TMPA)Cu^{I}]BAr^{F}: ^{1}H-NMR (DMSO-d_6): 8.62 (d, 4.44 Hz, 2H), 7.78 (dt, 1.76 Hz, 6.88 Hz, 2H), 7.73 (t, 7.72 Hz, 1H), 7.43 (d, 7.84 Hz, 2H), 7.34 (dt, 1.2 Hz, 6 Hz, 2H), 7.27 (t, 8.24 Hz, 2H), 4.12 (s, 2H), 4.09 (s, 4H), 2.70 (s, 3H).

Calcd for $C_{43}H_{20}N_4BCuF_{20}$: C, 49.33; H, 1.93; N, 5.35. Found: C, 48.79; H, 1.91; N 5.33.

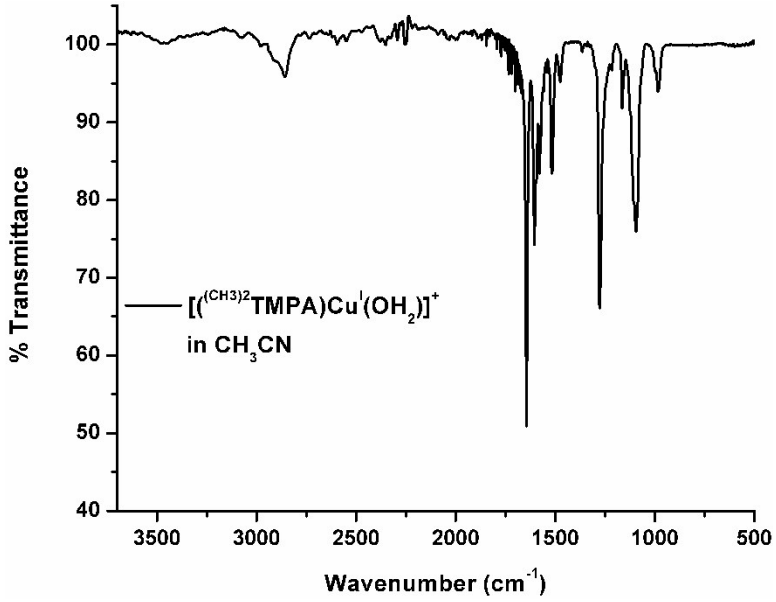
IR (CH_3CN):



[($^{(CH3)2}$TMPA)Cu^{I}(OH_2)]BAr^{F}: ^{1}H-NMR (DMSO-d_6): 8.70 (d, 2.28 Hz, 1H), 7.80 (t, 7.76 Hz, 1H), 7.75 (t, 7.76 Hz, 2H), 7.45 (d, 7.72 Hz, 1H), 7.37 (d, 5.88 Hz, 1H), 7.33 (d, 8 Hz, 2H), 7.25 (d, 7.44 Hz, 2H), 4.17 (s, 4H), 4.15 (s, 2H), 2.77 (s, 6H).

Calcd for $C_{44}H_{24}N_4BCuF_{20}O$: C, 48.98; H, 2.24; N, 5.19. Found: C, 48.65; H, 2.06; N, 4.57.

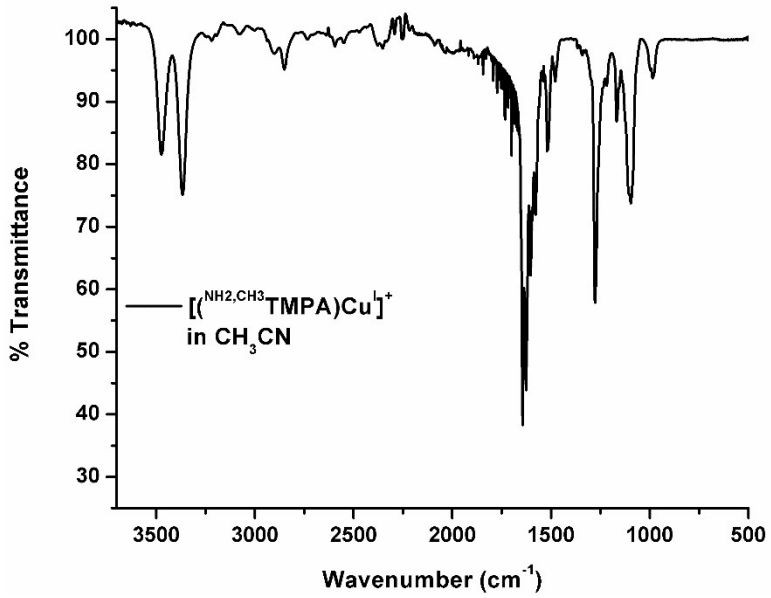
IR (CH_3CN):



[(^{NH2,CH3}TMPA)Cu^{I}]BAr^{F}: ^{1}H-NMR (DMSO-d_6): 8.77 (d, 4.12 Hz, 1H), 7.81 (dt, 1.68 Hz, 8.16 Hz, 1H), 7.71 (t, 7.64 Hz, 1H), 7.45 (d, 7.72 Hz, 1H), 7.39 (m, 2H), 7.28 (d, 7.48 Hz, 1H), 7.22 (d, 7.72 Hz, 1H), 6.59 (s, 1H), 6.48 (t, 5.24 Hz, 2H), 4.12 (s, 2 H), 4.08 (s, 2H), 3.84 (s, 2H), 2.74 (s, 3H).

Calcd for $C_{43}H_{21}N_5BCuF_{20}$: C, 48.63; H, 1.99; N, 6.59. Found: C, 48.36; H, 2.21; N, 6.20.

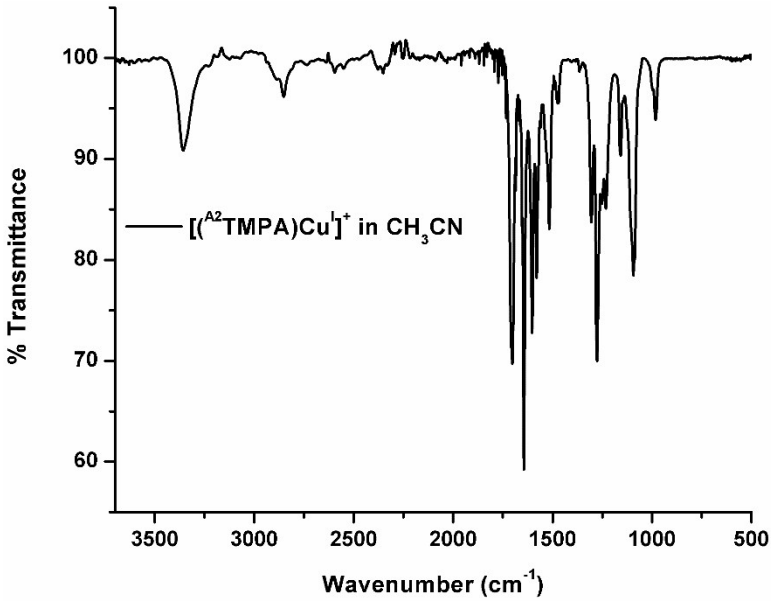
IR (CH_3CN): N–H stretches 3474 and 3368 cm^{-1}.



[(^{A2}TMPA)Cu^{I}]BAr^{F}: ^{1}H-NMR (DMSO-d_6): 10.56 (s, 1 H), 8.67 (d, 4.64 Hz, 2 H), 7.79 (td, 7.72 Hz, 1.68 Hz, 2 H), 7.62 (s, 1 H), 7.60 (s, 1 H), 7.39 (m, 2 H), 7.31 (d, 7.88 Hz, 2 H), 7.13 (m, 1 H), 4.05 (s, 4 H), 4.03 (s, 2 H), 2.14 (s, 3H).

Calcd for $C_{44}H_{22}N_4BCuF_{20}$: C, 48.48; H, 1.94; N, 6.43. Found: C, 48.42; H, 2.16; N, 6.21.

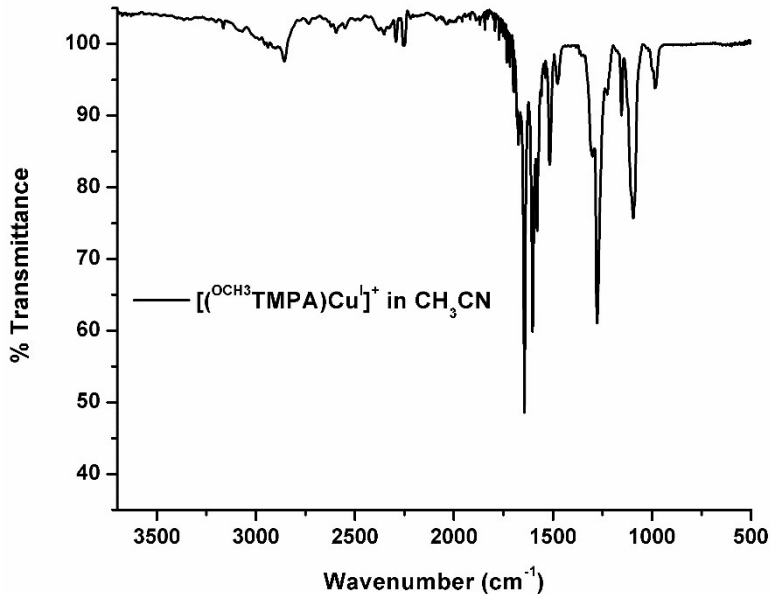
IR (CH_3CN): N–H stretch 3357 cm^{-1}; amide carbonyl stretch, 1702 cm^{-1}.



[(^{OCH3}TMPA)Cu^{I}]BArF•2H_2O: ^{1}H-NMR (DMSO-d_6): ^{1}H NMR (DMSO-d_6): 8.70 (d, 4.92 Hz, 2H), 7.90 (td, 7.72 Hz, 1.64 Hz, 2H), 7.72 (t, 8.32 Hz, 1H), 7.48 (m, 4H), 7.08 (d, 6.8 Hz, 1H), 6.79 (d, 8.36 Hz, 1H), 4.11 (s, 2H), 4.09 (s, 4H), 3.92 (s, 3H).

Calcd for $C_{43}H_{24}N_4BCuF_{20}O_3$: C, 46.99; H, 2.20; N, 5.10. Found: C, 46.31; H, 2.08; N, 4.95.

IR (CH_3CN):



[(^{NH2,CH3}TMPA)Cu^{II}(N_3^-)](ClO_4) complex:

In the open air, the ligand (^{NH2,CH3}TMPA, typically 35-50 mg, 0.11-0.16 mmol) was dissolved in 5 mL of CH_3OH in a 20 mL scintillation vial equipped with a stir bar. An equimolar amount of solid [Cu^{II}(ClO_4)$_2$]•(H_2O)$_6$ was added to the stirring solution, resulting in an immediate color change to blue. After stirring for 15 minutes, 1.1 equivalents of solid NaN_3 was added to the stirring solution, resulting in an immediate color change to dark

green and the formation of a precipitate. After stirring for 1 hour and 15 minutes, the reaction mixture was filtered through a short-stem pipette filled with celite with a cotton plug. The green filtrate was concentrated to give a green oil. This oil was dissolved in minimal methanol and layered with ether, resulting in a green powder.

[(^{NH2,CH3}TMPA)$Cu^{II}(N_3)$]ClO_4•H_2O: UV-vis (RT, CH_3CN): λmax = 397 nm (ε = 1970 $M^{-1}cm^{-1}$), 677 nm (ε = 235 $M^{-1}cm^{-1}$), 858 nm (sh, ε = 180 $M^{-1}cm^{-1}$).

Calcd for $C_{19}H_{23}N_8ClCuO_5$: C, 42.07; H, 4.27; N, 20.66. Found: C, 42.64; H, 3.97; N, 21.16.

III. Infrared spectroscopy of [(^{X}TMPA)$Cu^{II}(N_3^-)$]ClO_4 complexes:

The azido complexes [(^{X}TMPA)$Cu^{II}(N_3)$]ClO_4 were dissolved in CH_3CN to give a 50 mM solution. This solution was injected into the solution IR cell to record the spectra. A blank spectrum of CH_3CN was also taken and used to subtract out the solvent absorbance.

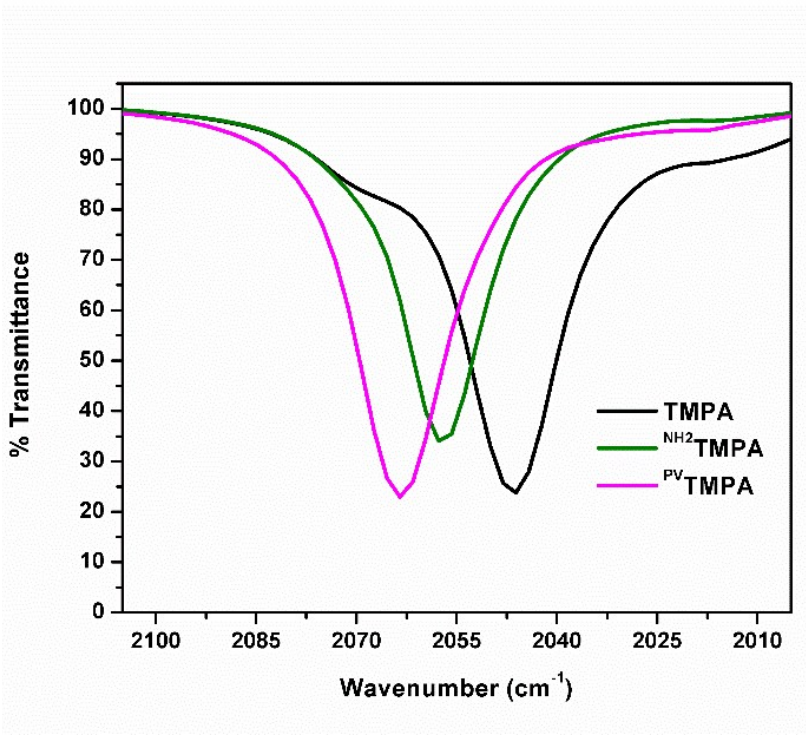


Figure S2. Infrared spectra of the $[(^{X}TMPA)Cu^{II}(N_3^-)]^+$ complexes in MeCN, zoomed in to emphasize the position of the $\nu_{N\text{-}N}$ stretch of the azido ligand. $[(^{PV}TMPA)Cu^{II}(N_3)]ClO_4$ (**magenta**); $[(^{NH2}TMPA)Cu^{II}(N_3)]ClO_4$ (**green**); $[(TMPA)Cu^{II}(N_3)]ClO_4$ (**black**).

Table S1. ν(N-N) stretching frequencies for [(^{X}TMPA)Cu^{II}(N_3^-)]ClO_4 complexes in CH_3CN. As evidenced by comparing the ν(N-N) values for ^{NH2}TMPA and TMPA *vs.* ^{NH2,CH3}TMPA and ^{CH3}TMPA, the ^{NH2}TMPA and ^{NH2,CH3}TMPA ligands have the same H-bonding capabilities (as evidenced by their 10 cm^{-1} blue-shift when compared to their respective "base" ligand).

Complex	ν_{N-N} (cm^{-1})	$\nu_L - \nu_{TMPA}$	$\nu_L - \nu_{CH3TMPA}$
[Cu^{II}(TMPA)(N_3^-)]ClO_4	2047	0	-
[Cu^{II}(^{NH2}TMPA)(N_3^-)]ClO_4	2057	10	4
[Cu^{II}($^{(NH2)2}$TMPA)(N_3^-)]ClO_4	2065	18	12
[Cu^{II}($^{(CH3)}$TMPA)(N_3^-)]ClO_4	2053	6	0
[Cu^{II}(^{NH2,CH3}TMPA)(N_3^-)]ClO_4	2063	16	10
[Cu^{II}(^{PV}TMPA)(N_3^-)]ClO_4	2064	17	11

IV. Cyclic Voltammetry of the [(^{X}TMPA)Cu^{I}]BArF complexes

All cyclic voltammograms were collected under an inert (Ar) atmosphere in CH_3CN at 20 ^{o}C. The concentration of the [(^{X}TMPA)Cu^{I}]BArF complexes was ~0.5 mM, with $TBAPF_6$ used as the supporting electrolyte (0.1 M concentration). A three-electrode system was used, as follows: $Ag/AgNO_3$ (10 mM) in CH_3CN as reference electrode; glassy carbon electrode as the working electrode; platinum wire as the counter electrode. All reduction potentials were referenced *vs.* $Fc^{+/0}$ as an external standard under the same conditions as the [(^{X}TMPA)Cu^{I}]BArF complexes.

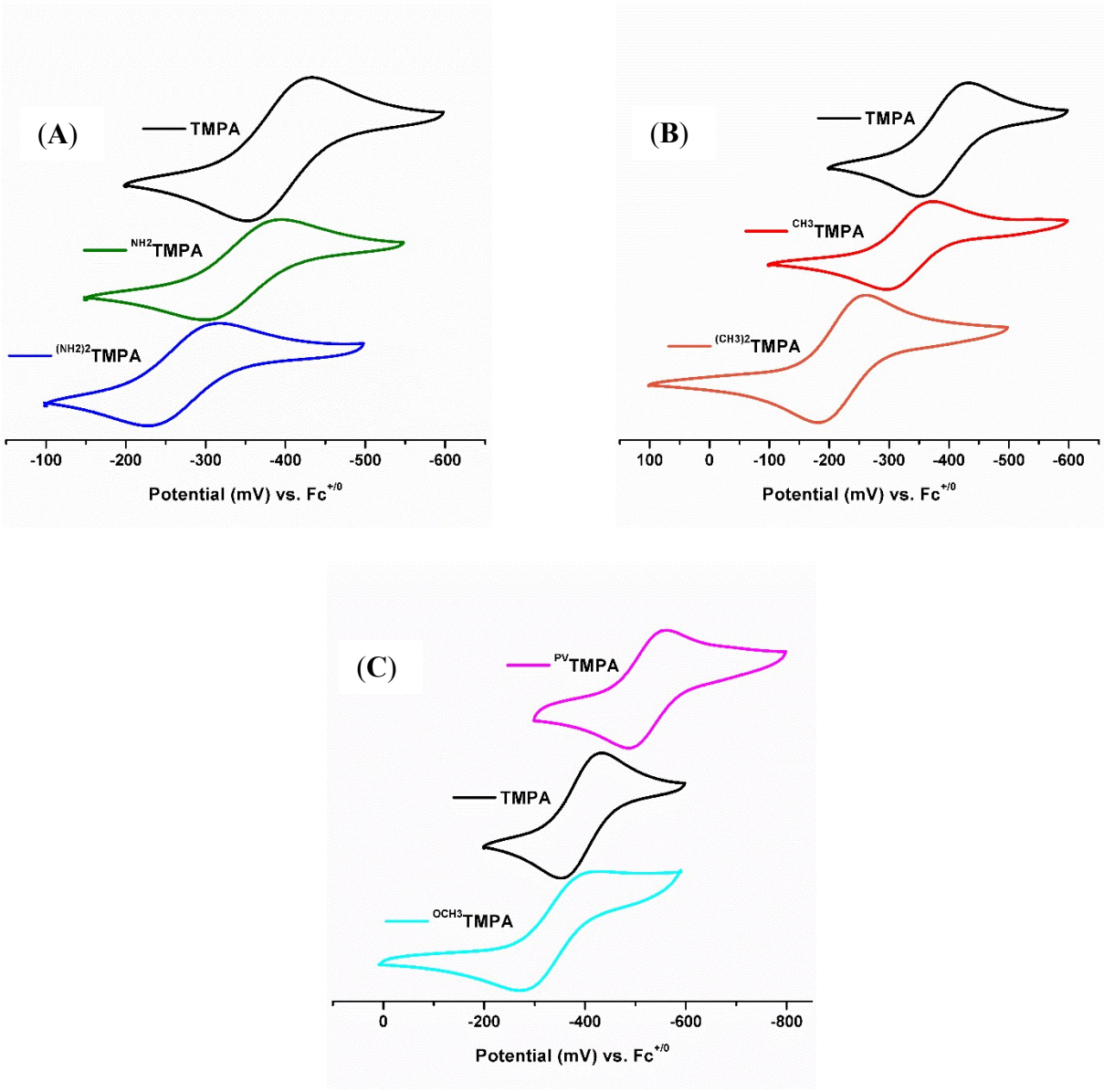


Figure S3. Cyclic voltammograms of the $[(^{X}TMPA)Cu^{I}]^{+}$ complexes in MeCN at room temperature. (**A**) $^{X}TMPA$ = TMPA (**black**), $^{NH2}TMPA$ (**green**), $^{(NH2)2}TMPA$ (**blue**). (**B**) $^{X}TMPA$ = TMPA (**black**), $^{CH3}TMPA$ (**orange**), $^{(CH3)2}TMPA$ (**red**). (**C**) $^{X}TMPA$ = $^{PV}TMPA$ (**magenta**), TMPA (**black**), $^{OCH3}TMPA$ (**teal**).

Table S2. $Cu^{II/I}$ reduction potentials determined for [(^{X}TMPA)Cu^{I}]BAr^{F} complexes in CH_3CN at room temperature, using $TBAPF_6$ as the supporting electrolyte.

Ligand (^{X}TMPA)	$E_{1/2}$ (mV)
TMPA	–405
^{NH2}TMPA	–350
$^{(NH2)2}$TMPA	–275
^{CH3}TMPA	–340
$^{(CH3)2}$TMPA	–225
^{PV}TMPA	–520
^{OCH3}TMPA	–350

V. UV-vis spectroscopy monitoring formation of HS and LS heme-peroxo-copper complexes:

HS-^{X}TMPA complexes were generated by taking a 2-methyltetrahydrofuran (MeTHF) solution containing 2.7 mL of an equimolar (0.1 mM) mixture of F_8Fe^{II} and [Cu^{I}(^{X}TMPA)](BArF) in a 10 mm path length quartz Schlenk cuvette that was prepared in a glovebox and sealed with a rubber septum before being cooled in the cryostat chamber to –90ºC. Dioxygen was bubbled through the solution until full formation of the high-spin species was observed, i.e., no further spectroscopic changes occurred. After dioxygen was added, vacuum/Ar bubbling cycles were performed to remove excess O_2. For low-spin complexes, after generation of the analogous high-spin species, **HS-^{X}TMPA,** at –

90ºC, 25 µL of a solution containing 1 equiv. of DCHIm were added to generate the **LS-^{X}TMPA**. Soret measurements were done at 0.01 mM of F_8Fe^{II} and [Cu^{I}(^{X}TMPA)](BArF).

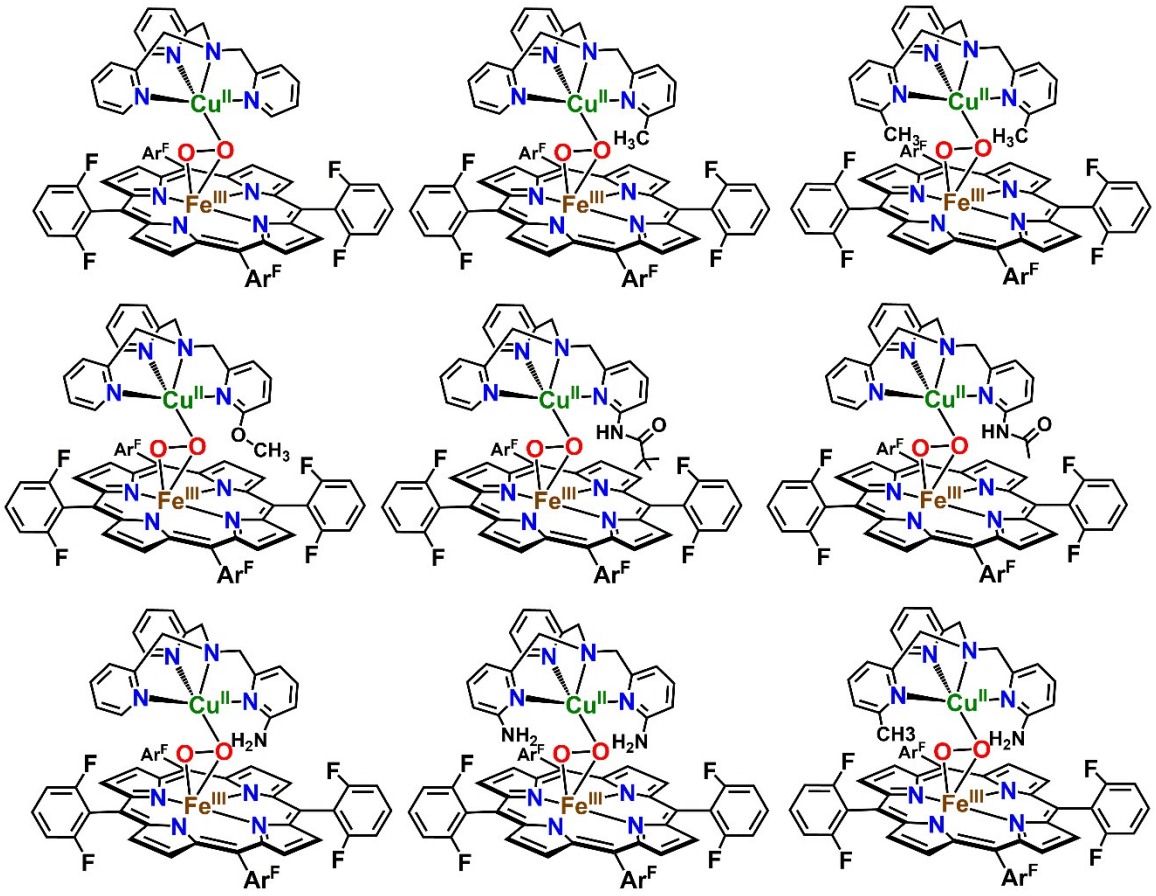
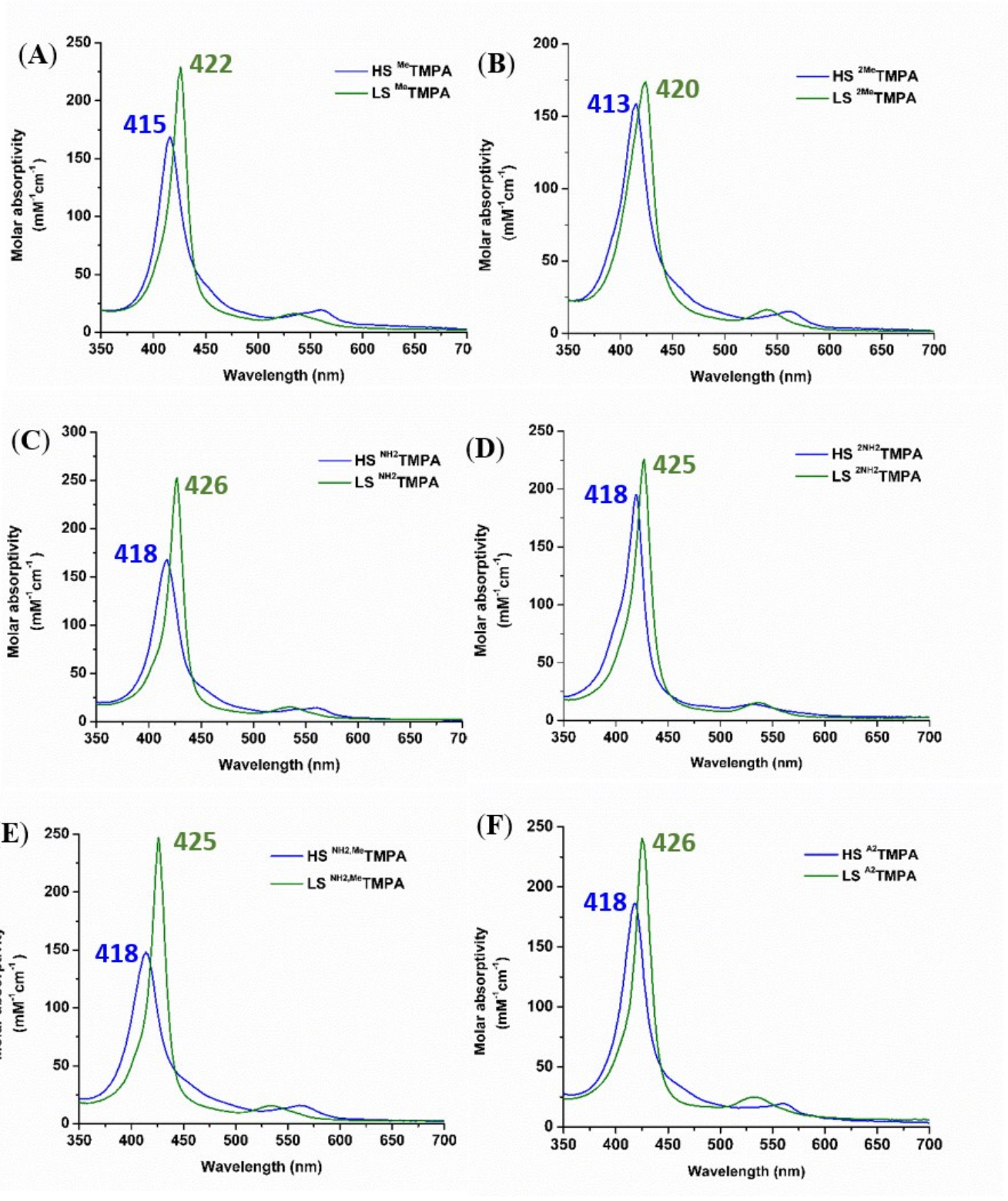


Figure S4. Eight novel high spin heme-peroxo-copper complexes bearing derivatized TMPA-based copper chelates prepared in this work and whose UV-vis spectra are shown below.


(A)
422
415
HS Me TMPA
LS Me TMPA
Molar absorptivity (mM-1cm-1)
Wavelength (nm)
(B)
420
413
HS 2Me TMPA
LS 2Me TMPA
Molar absorptivity (mM-1cm-1)
Wavelength (nm)
(C)
426
418
HS NH2 TMPA
LS NH2 TMPA
Molar absorptivity (mM-1cm-1)
Wavelength (nm)
(D)
425
418
HS 2NH2 TMPA
LS 2NH2 TMPA
Molar absorptivity (mM-1cm-1)
Wavelength (nm)
(E)
425
418
HS NH2,Me TMPA
LS NH2,Me TMPA
Molar absorptivity (mM-1cm-1)
Wavelength (nm)
(F)
426
418
HS A2 TMPA
LS A2 TMPA
Molar absorptivity (mM-1cm-1)
Wavelength (nm)

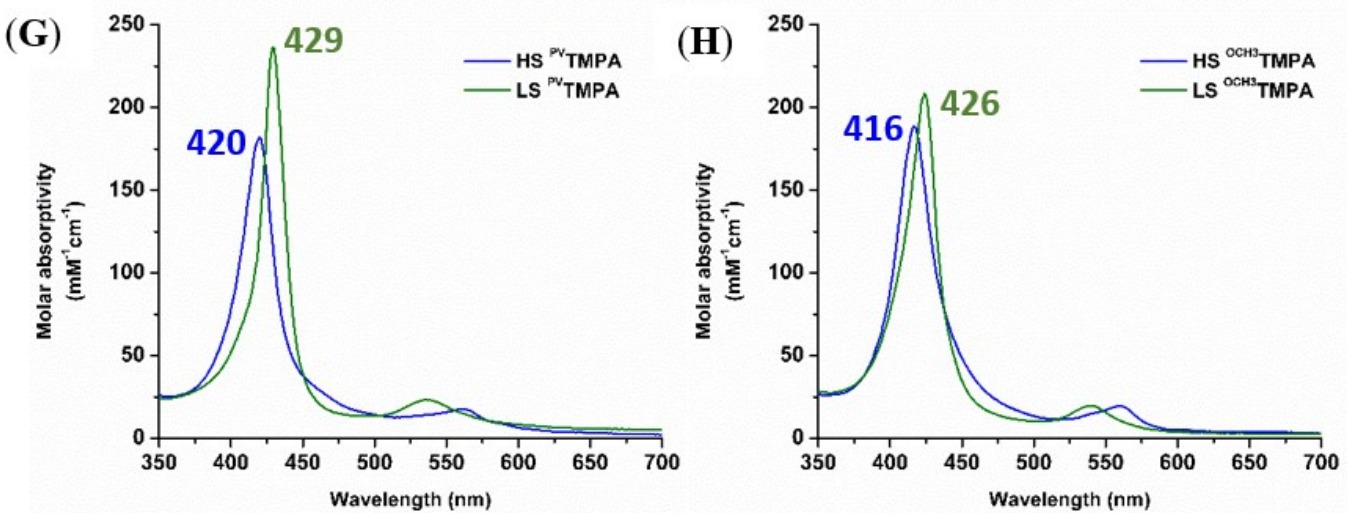
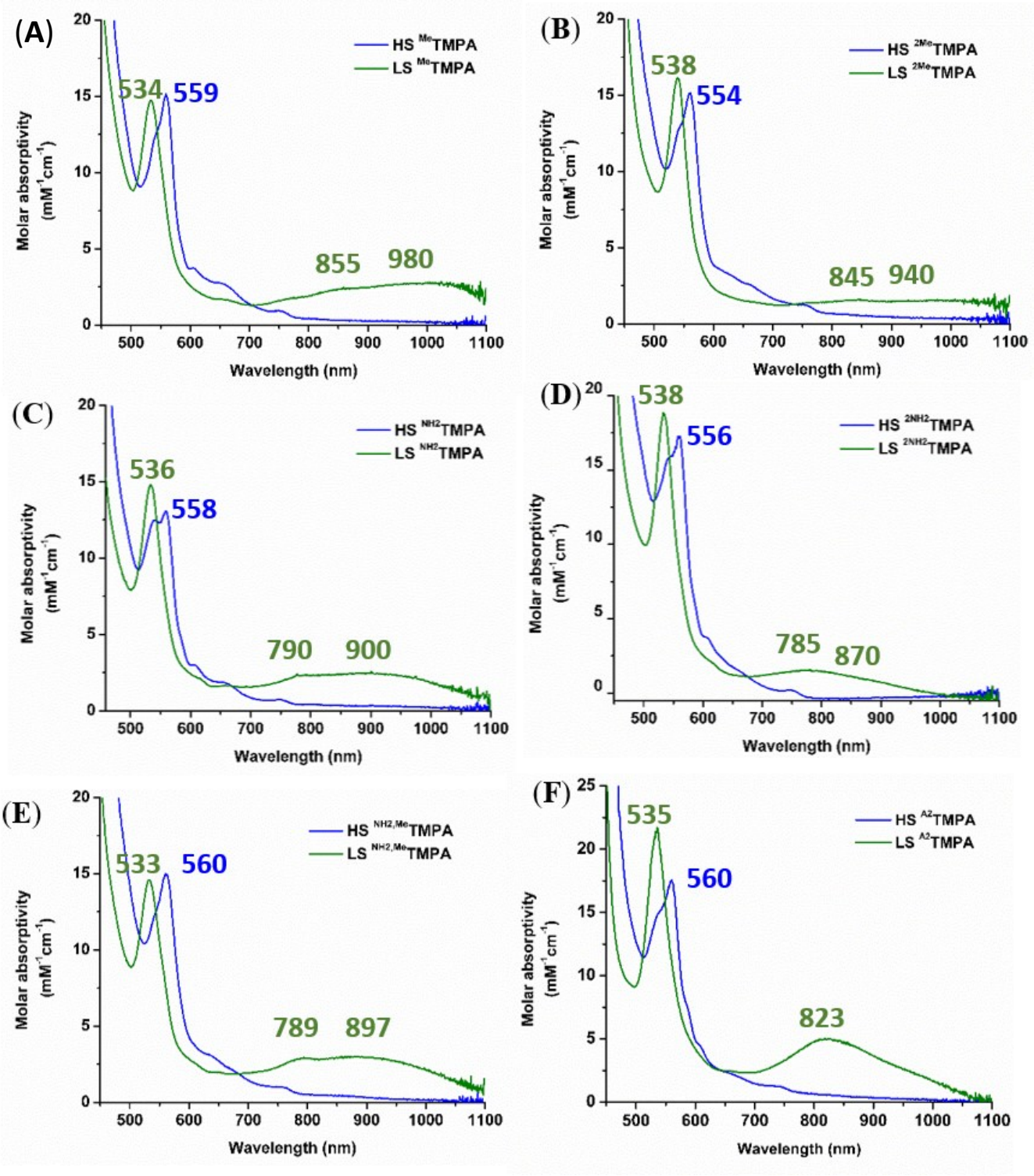


Figure S5. UV-vis spectra at 0.01 mM for the high- (blue spectrum) and low (green spectrum) -spin heme-peroxo-copper complexes with various TMPA derivative ligands for copper in MeTHF at -90 °C. The low-spin species are shown in green, displaying unique low-energy regions. (**A**) L = ^{CH3}TMPA; (**B**) L = $^{(CH3)2}$TMPA; (**C**) L = ^{NH2}TMPA; (**D**) L = $^{(NH2)2}$TMPA; (**E**) L = ^{NH2,CH3}TMPA (**F**) L = ^{A2}TMPA (**G**) L = ^{PV}TMPA (**H**) L = ^{OMe}TMPA.


(A)
HS Me TMPA
LS Me TMPA
534
559
855
980
(B)
HS 2Me TMPA
LS 2Me TMPA
538
554
845
940
(C)
HS NH2 TMPA
LS NH2 TMPA
536
558
790
900
(D)
HS 2NH2 TMPA
LS 2NH2 TMPA
538
556
785
870
(E)
HS NH2,Me TMPA
LS NH2,Me TMPA
533
560
789
897
(F)
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535
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823
Molar absorptivity (mM-1cm-1)
Wavelength (nm)

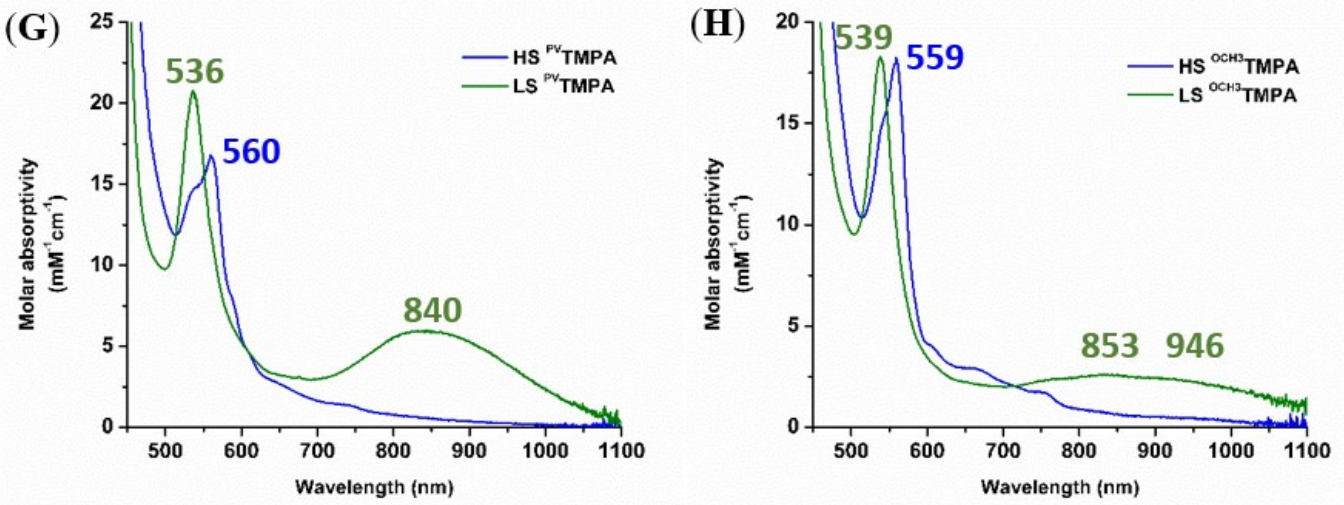


Figure S6. UV-vis spectra at 0.1 mM for the high- (blue spectrum) and low (green spectrum) -spin heme-peroxo-copper complexes with various TMPA derivative ligands for copper in MeTHF at -90 °C. The low-spin species are shown in green, displaying unique low-energy regions. (**A**) L = ^{CH3}TMPA; (**B**) L = $^{(CH3)2}$TMPA; (**C**) L = ^{NH2}TMPA; (**D**) L = $^{(NH2)2}$TMPA; (**E**) L = ^{NH2,CH3}TMPA (**F**) L = ^{A2}TMPA (**G**) L = ^{PV}TMPA (**H**) L = ^{OMe}TMPA.

VI. EPR spectroscopy of HS and LS heme-peroxo-copper complexes:

HS-^{X}TMPA complexes were generated by bubbling 5 mL of dioxygen through a MeTHF solution containing an equimolar (1 mM) mixture of F_8Fe^{II} and [Cu^{I}(^{X}TMPA)](BArF) (total volume = 0.6 mL) at –90 ºC (acetone/liquid N_2 bath) in a 5 mm outer diameter quartz EPR tube. In each case, after addition of dioxygen, the solution was bubbled with Ar for 60 s to remove excess O_2. For low-spin complexes, after generation of the analogous high-spin species, **HS-^{X}TMPA,** at –90ºC, 25 µL of a solution containing 1 equiv. of DCHIm were added to generate the **LS-^{X}TMPA**. After complexes were generated, tubes were frozen in $N_{2(liq)}$, and all spectra were recorded at 10 K. All HS and LS complexes were EPR silent (X-band) consistent with anti-ferromagnetic coupling between the iron and copper moieties.

VII. ^{2}H-NMR spectroscopy of LS heme-peroxo-copper complexes

The high-spin and low-spin complexes with ^{X}TMPA ligation were generated using the pyrrole-deuterated porphyrin, F_8-d_8,[2] and 1 eq of the ^{X}TMPACu(I)BarF complex at 5.0 mM concentrations in MeTHF with a total volume of 0.6 mL at –90°C (acetone/liq. N_2 bath) in a 9-inch, 5 mm, rubber septum-capped, NMR tube. Oxygen was added to the reduced complexes via bubbling needle, followed by bubbling with Ar to remove excess oxygen.[11] LS complexes were generated by adding 1 eq of DCHIm to the purged mixture and mixing with Ar. ^{2}H NMR spectra were acquired on a Bruker AVANCE 300 MHz NMR spectrometer at 46.072 MHz. Experiments were carried out at –90°C using a recycle delay of 0.01s and total of 5120 scans were collected. The peaks were referenced to the MeTHF solvent peak at 1.2 ppm (the -CH_3 group of MeTHF, which is the most upfield). The HS (99 ppm) and LS (5 ppm) parent TMPA complexes was previously reported by Karlin and coworkers. Some spectra have the previously reported (MeTHF)$F_8Fe^{III}(O_2^{\bullet-})$ (9.2 ppm) as a minor impurity.[11,12]

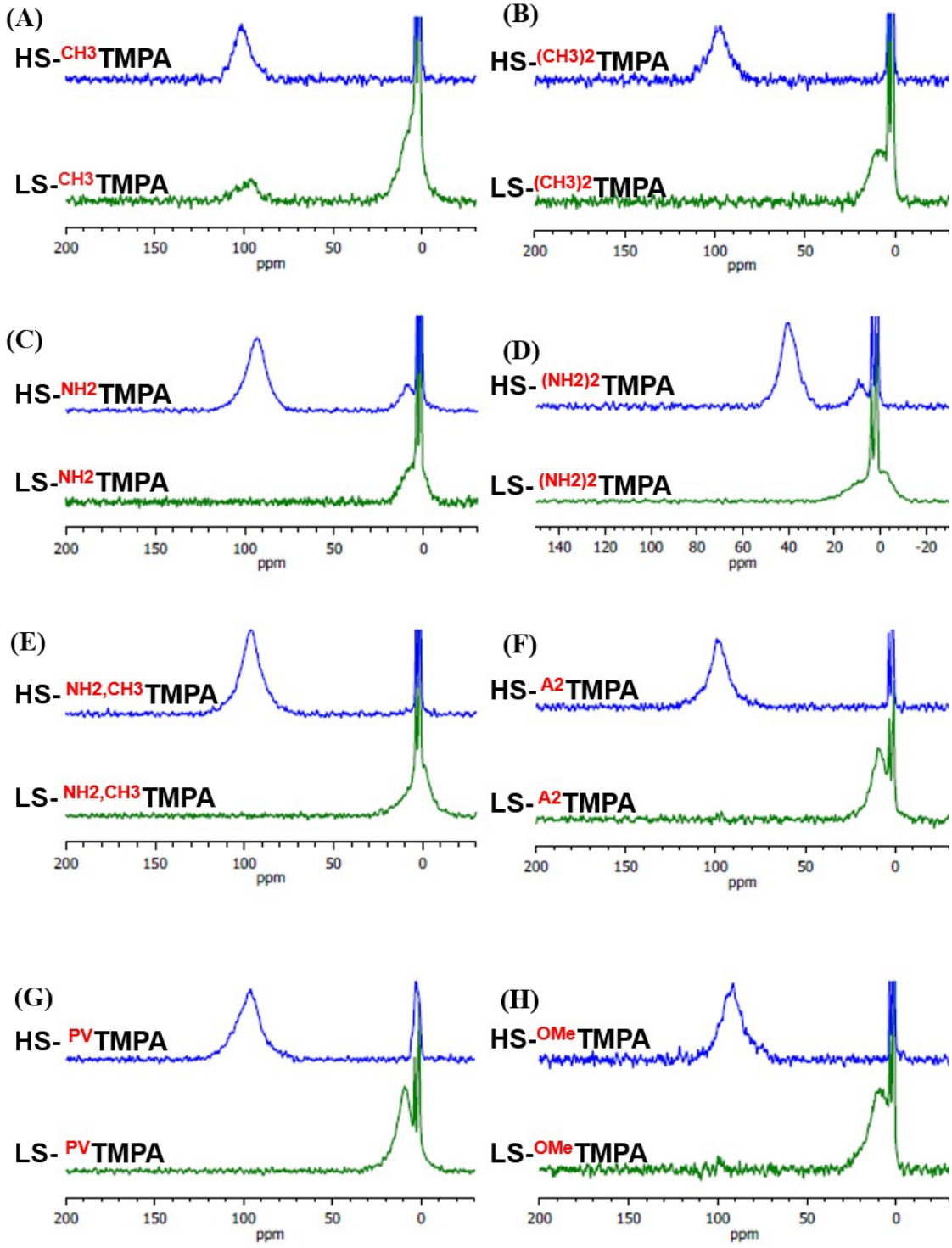


Figure S7. ^{2}H-NMR spectra (-90 ^{o}C) of (HS-^{X}TMPA) (**blue spectra**) and (LS-^{X}TMPA) (**green spectra**) at 5 mM in MeTHF. (**A**) L = ^{CH3}TMPA; (**B**) L = $^{(CH3)2}$TMPA; (**C**) L = ^{NH2}TMPA; (**D**) L = $^{(NH2)2}$TMPA; (**E**) L = ^{NH2,CH3}TMPA (**F**) L = ^{A2}TMPA (**G**) L = ^{PV}TMPA (**H**)

L = ^{OCH3}TMPA. Note that in spectra for the HS complexes in (**C**) and (**D**) there is a minor impurity that has been previously reported as (MeTHF)$F_8Fe^{III}(O_2^{\bullet-})$ (at 9.2 ppm).[11,12]

VIII. Resonance Raman spectroscopy of LS heme-peroxo-copper complexes

The high-spin and low-spin complexes with ^{X}TMPA ligation were generated in the same fashion as EPR samples, above, at 1.0 mM concentrations with a total volume of 0.6 mL at –90°C (acetone/liq. N_2 bath) in a 9-inch, 5 mm, rubber septum-capped, NMR tube using either $^{16}O_2$ or $^{18}O_2$ and mixed by bubbling Ar.[11,12] The tubes were then frozen and flame-sealed. Spectra were obtained with spinning tubes at 77 K with $\lambda_{excit.}$ = 413 nm unless otherwise noted.

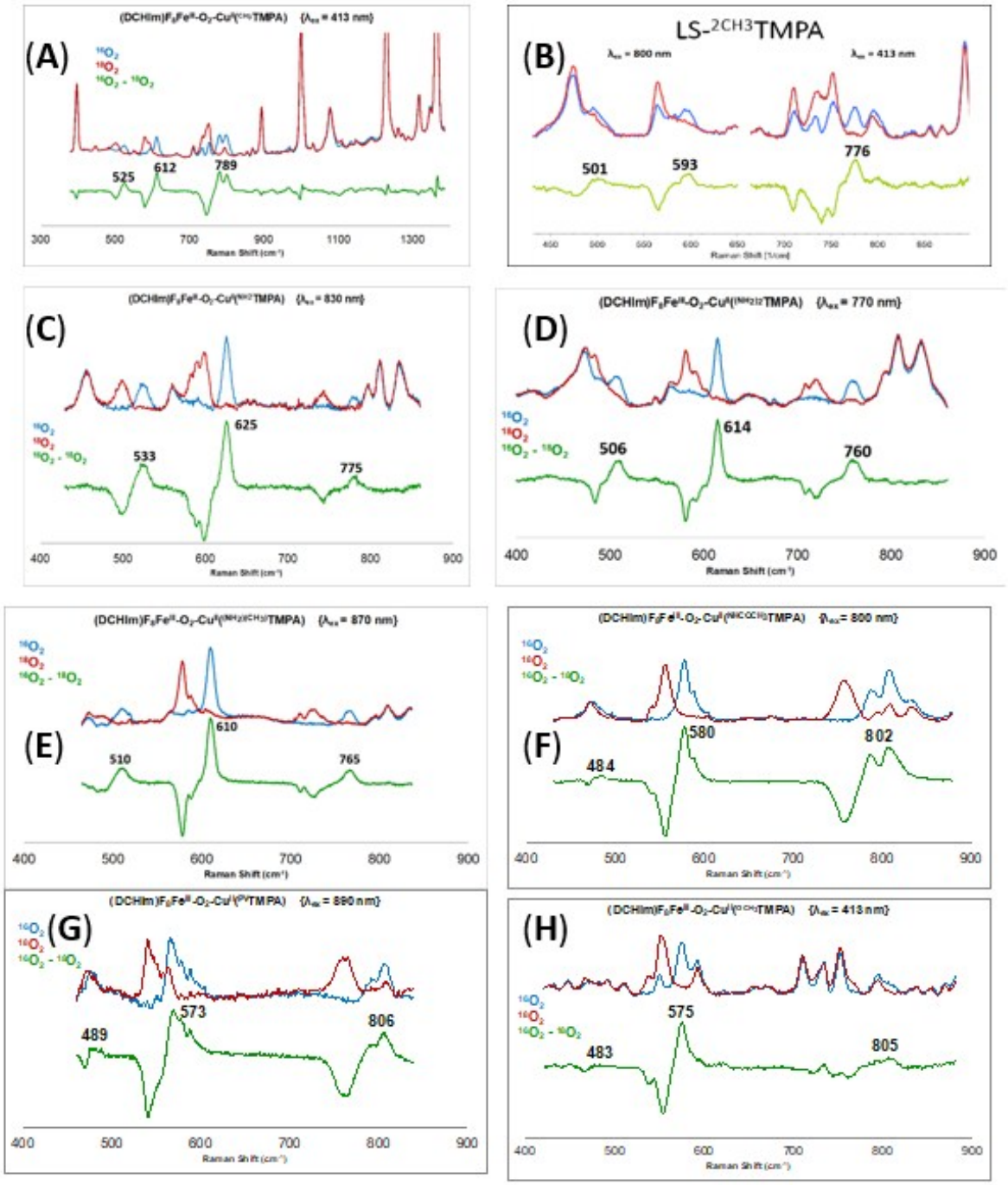


Figure S8. Resonance Raman spectra of (LS-^{X}TMPA) ($^{16}O_2$: blue; $^{18}O_2$: red; $^{16}O_2$-$^{18}O_2$: green spectra) by bubbling dioxygen into a solution of 1 mM (MeTHF)$_2$(d_8-F_8)Fe^{II} and 1 equiv. [(^{X}TMPA)Cu^{I}]BArF in MeTHF at -90 ^{o}C followed by addition of 1 eq DCHIm. (**A**) L = ^{CH3}TMPA; (**B**) L = $^{(CH3)2}$TMPA; (**C**) L = ^{NH2}TMPA; (**D**) L = $^{(NH2)2}$TMPA; (**E**) L = ^{NH2,CH3}TMPA (**F**) L = ^{A2}TMPA (**G**) L = ^{PV}TMPA (**H**) L = ^{OMe}TMPA.

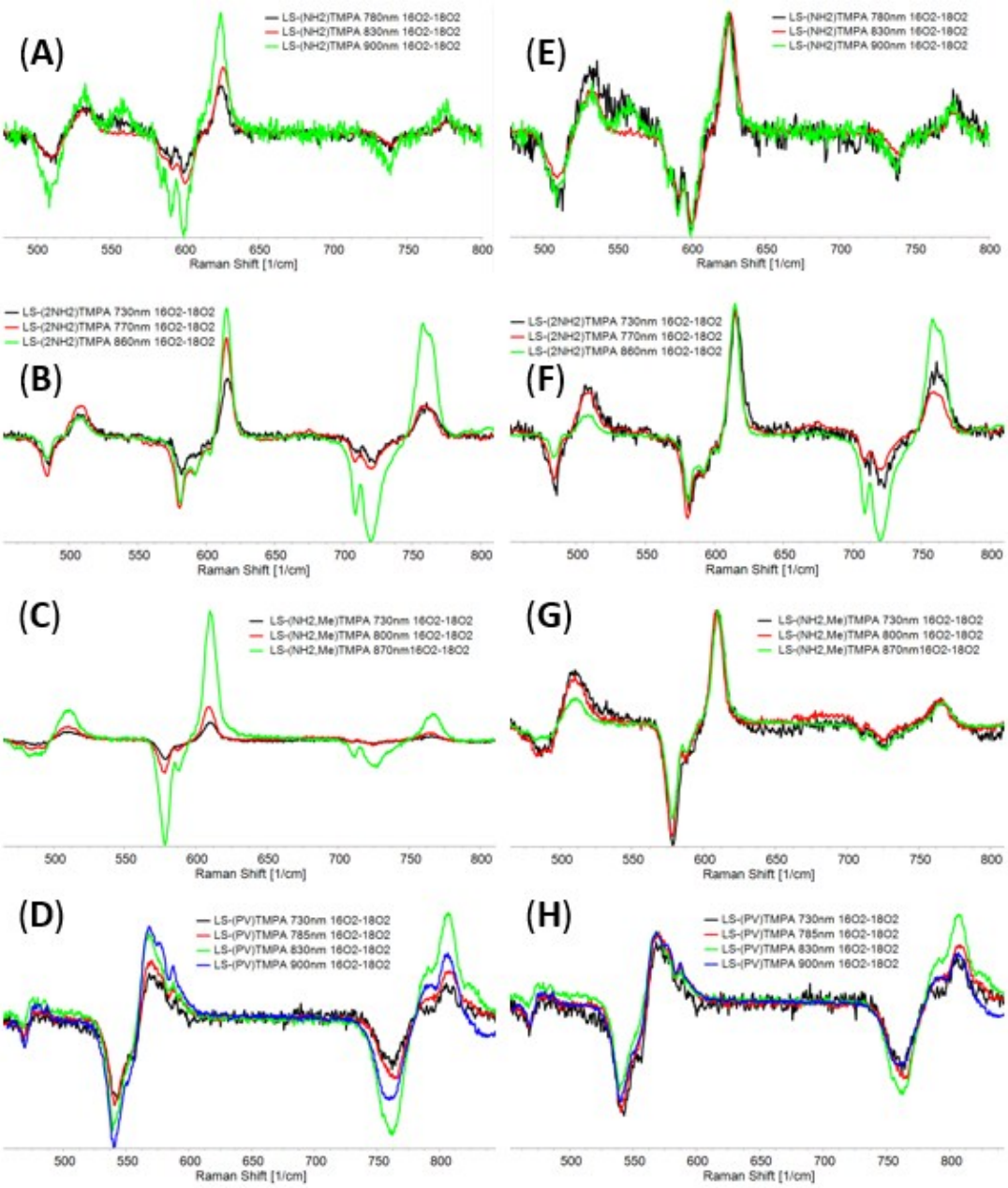


Figure S9. Resonance Raman $^{16}O_2$-$^{18}O_2$ difference spectra collected at various low-energy wavelengths (given in each figure) for H-bond-substituted complexes LS-^{NH2}TMPA, LS-$^{(NH2)2}$TMPA, LS-^{NH2,CH3}TMPA, and LS-^{PV}TMPA. Data in Figures A-D are normalized to the MeTHF solvent band at 810 cm^{-1} to show how enhancement varies with excitation. Data Figures E-H are normalized to the Fe-O intensity to show how relative enhancement of core modes (assigned as the Cu-O, Fe-O, and O-O, in order of increasing frequency) varies with excitation.

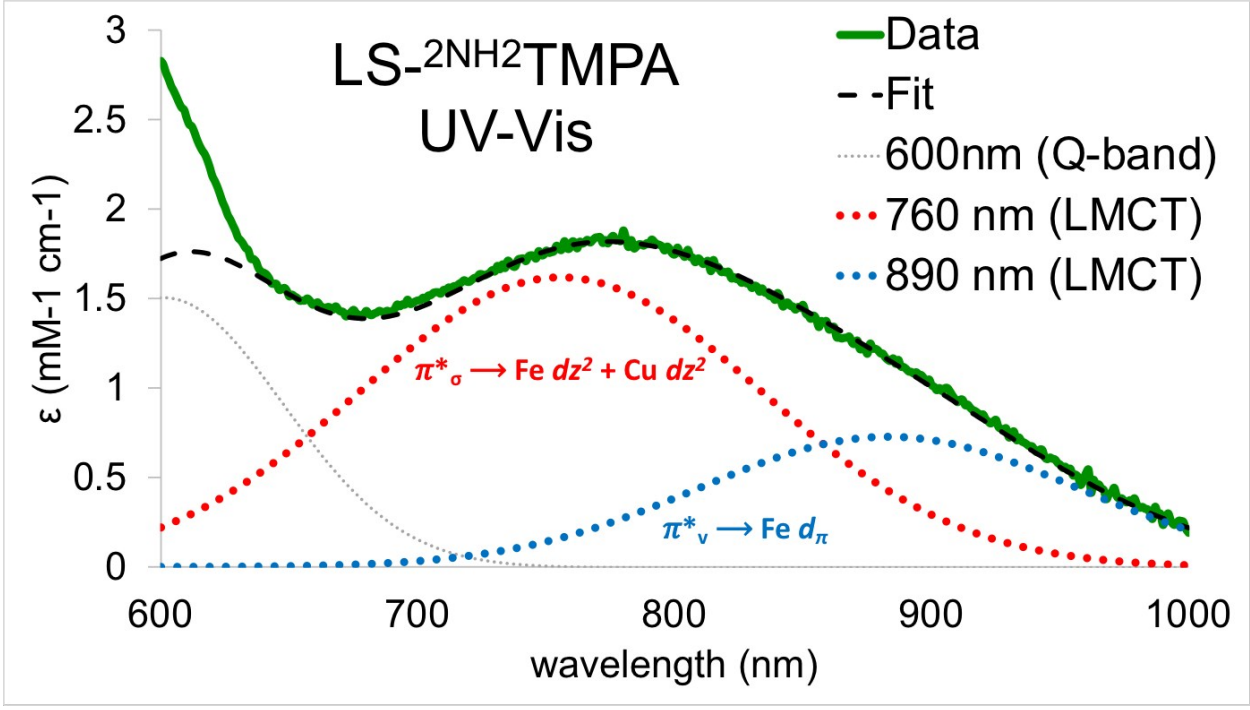


Figure S10. UV-Vis spectrum (green) for the complex **LS-$^{(NH2)2}$TMPA**, where the low energy region is fit to two distinct components (red curve with λ_{max} = 760 nm, and blue curve with λmax = 890 nm). As mentioned in the text, the rR data with low energy excitation (Figure S9) suggest that the higher energy transition has peroxo LMCT character involving both metals, while the lower energy transition has predominantly peroxo to Fe LMCT character.

IX. DFT Calculations

Density functional theory (DFT) calculations were performed with Gaussian09, version D.01 software package. All calculations were done using the B3LYP functional (including GD3BJ dispersion corrections), within the spin-unrestricted formalism and broken-symmetry singlet surface, employing a split basis set as follows: 6-311g* for Fe and Cu; 6-31++g** for all metal-bound N/O atoms and H-bonding H atoms, and 6-31g for all remaining atoms. Tight SCF convergence and an ultrafine integration grid were used. Cyclohexyl substituents on DCHIm ligands were

truncated as methyl groups in order to lower the computational cost. Free energies were calculated at 183 K. Unconstrained optimization yielded one minimum for each of the structures.

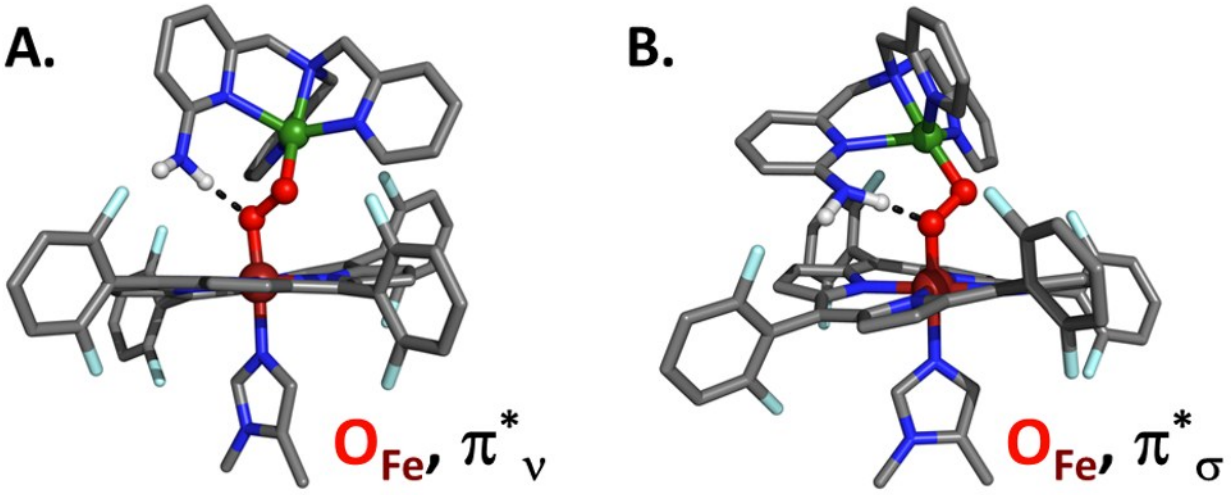


Figure S11. Optimized structures for LS-^{NH2}TMPA, differing by orientation of the H-bond to the peroxo ligand moiety. Structural parameters are given in Table S1. All structures were unconstrained to give no imaginary frequencies.

Table S3. Summary of DFT results for the possible structures of LS-^{NH2}TMPA shown in Figure S6. The Badger's rule-predicted frequency change ($\Delta\nu_{B.R.}$) is calculated using the optimized core bond lengths.

	LS-TMPA	**O_{Cu}, π^*_{ν}**	**O_{Fe}, π^*_{ν}**	**O_{Cu}, π^*_{σ}**	**O_{Fe}, π^*_{σ}**
ΔE [ΔG_{183K}] (kcal/mol)	-	0 [0]	+0.5 [+2.2]	+5.4 [+5.7]	+1.3 [+3.2]
$\Delta\nu$ (O–O) (cm^{-1})	[926]	-11	4	-16	-4
$\Delta\nu$ (Fe–O) (cm^{-1})	[642]	8	-10	18	-1
$\Delta\nu$ (Cu–O) (cm^{-1})	[549]	7	10	26	-10
***r*(O–O) (Å)**	1.406	1.419	1.416	1.413	1.414
***r*(Fe–O) (Å)**	1.797	1.794	1.809	1.797	1.803
***r*(Cu–O) (Å)**	1.874	1.879	1.868	1.867	1.882
$\Delta\nu_{B.R.}$(O–O) (cm^{-1}) [a]	-	-32	-25	-17	-20
$\Delta\nu_{B.R.}$ (Fe–O) (cm^{-1})	-	4	-14	0	-7
$\Delta\nu_{B.R.}$ (Cu–O) (cm^{-1})	-	-5	6	7	-8
r(N(H)...O) ν (Å)		2.758	2.836		
r(N(H)...O) σ (Å)				2.676	2.778

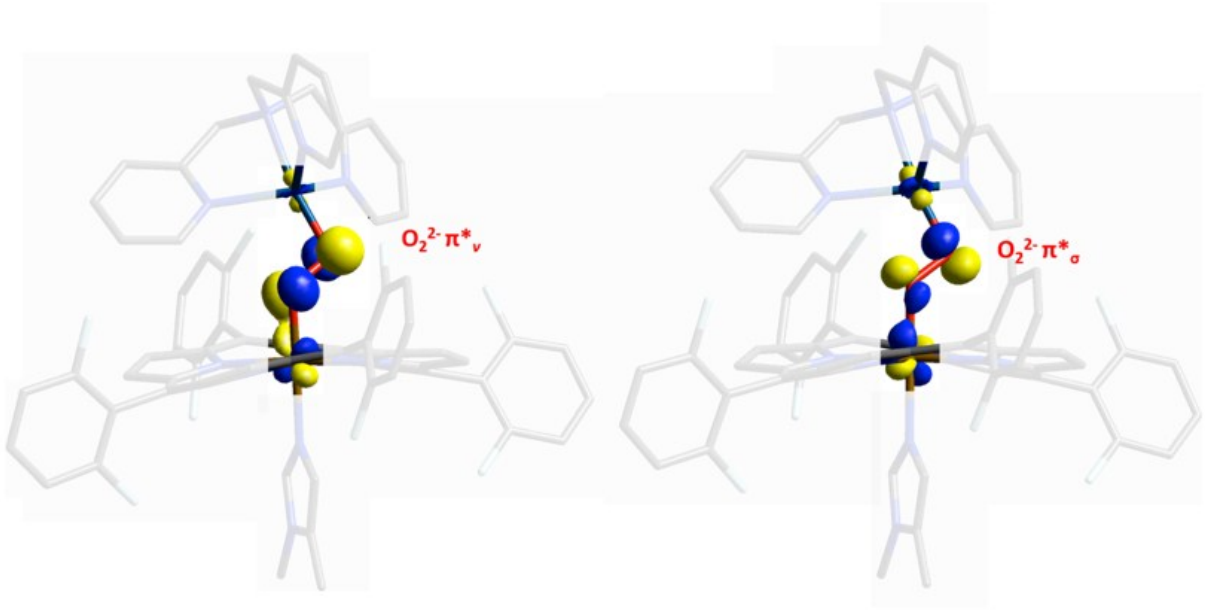


Figure S12. MO contour plots depicting the π^*_v and π^*_σ orbitals of the peroxo moiety referred to in the text.

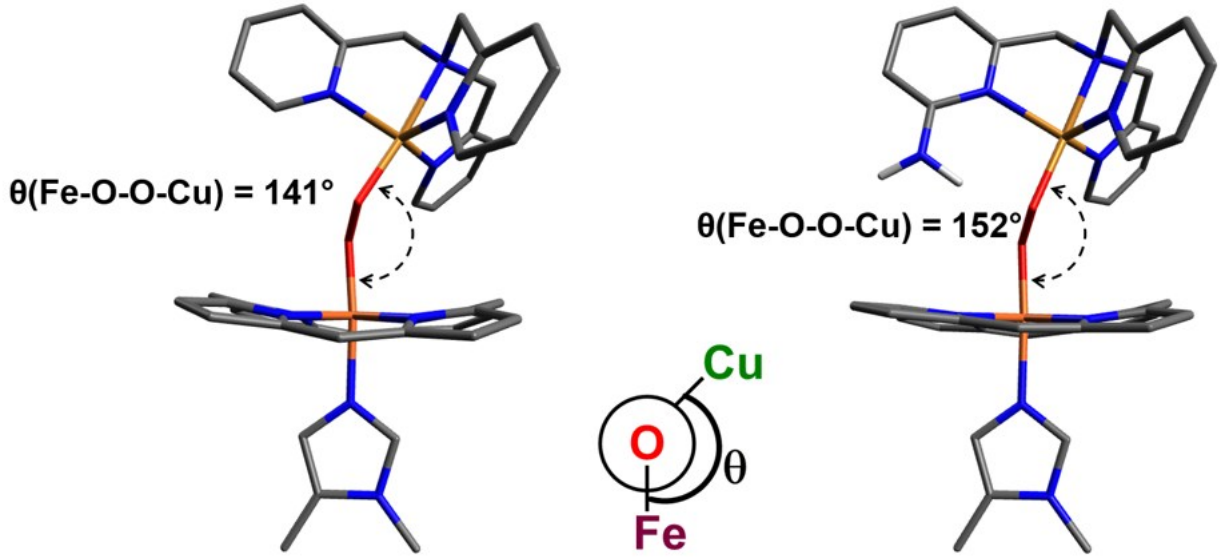


Figure S13. Emphasis of the change in the Fe-O-O-Cu dihedral angle for the optimized structures of (**A)** LS-TMPA and (**B**) LS-^{NH2}TMPA.

Table S4. Summary of DFT results for the possible structures of LS-$^{(NH2)2}$TMPA shown in Figure S9. The Badger's rule-predicted frequency change ($\Delta\nu_{B.R.}$) is calculated using the optimized core bond lengths.

	LS-TMPA	**O_{Cu}, O_{Fe}**	**O_{Cu}, O_{Cu}**
ΔE [ΔG_{183K}] (kcal/mol)	-	0 [0]	-0.4 [+0.5]
$\Delta\nu$ (O–O) (cm^{-1})	[926]	-34	-20
$\Delta\nu$ (Fe–O) (cm^{-1})	[642]	-18	-26
$\Delta\nu$ (Cu–O) (cm^{-1})	[549]	-40	-49
r(O–O) (Å)	1.406	1.426	1.423
r(Fe–O) (Å)	1.797	1.828	1.819
r(Cu–O) (Å)	1.874	1.914	1.919
$\Delta\nu_{B.R.}$(O–O) (cm^{-1}) [a]	-	-48	-41
$\Delta\nu_{B.R.}$ (Fe–O) (cm^{-1})	-	-36	-26
$\Delta\nu_{B.R.}$ (Cu–O) (cm^{-1})	-	-39	-43

Analysis of electronic vs. structural H-bonding effects for LS-^{NH2}TMPA

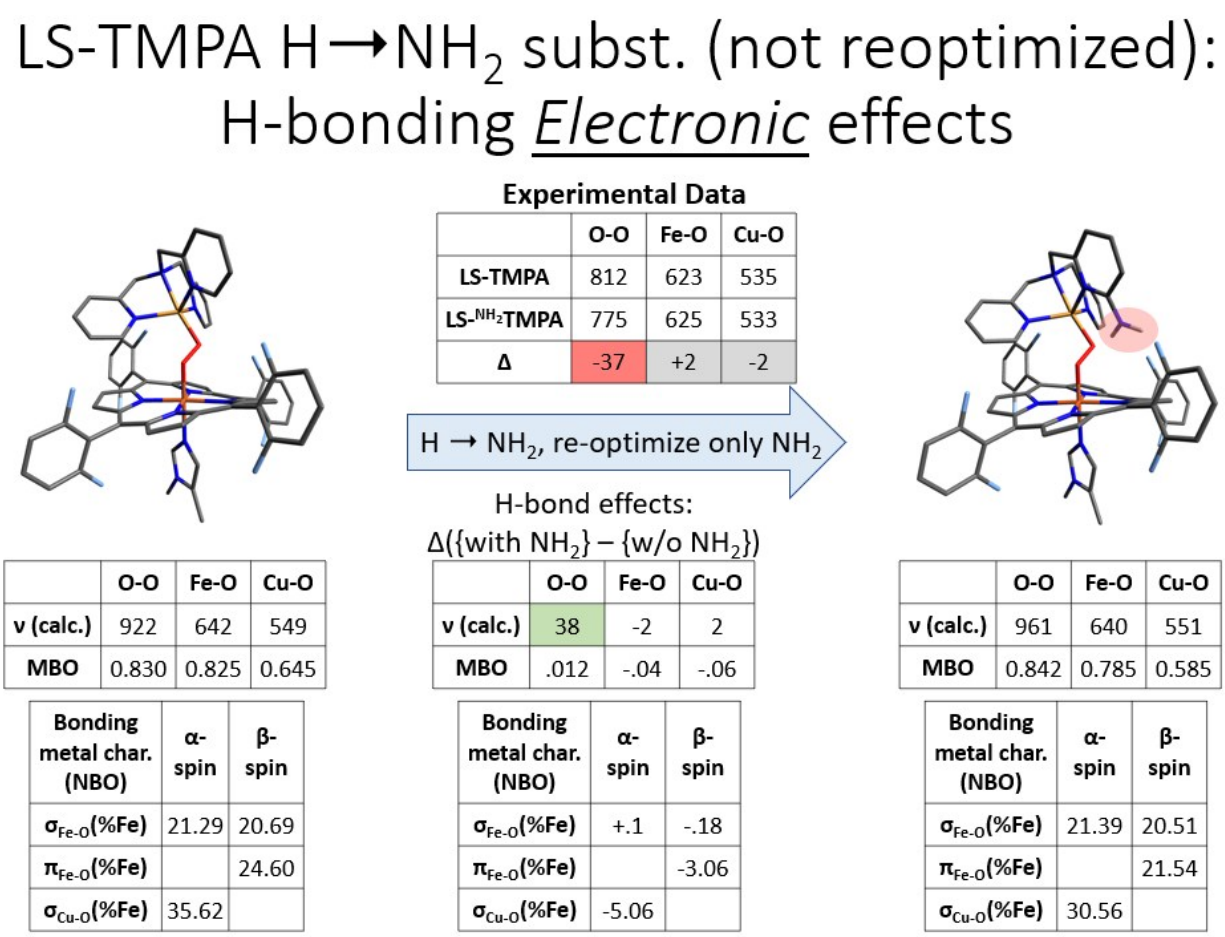
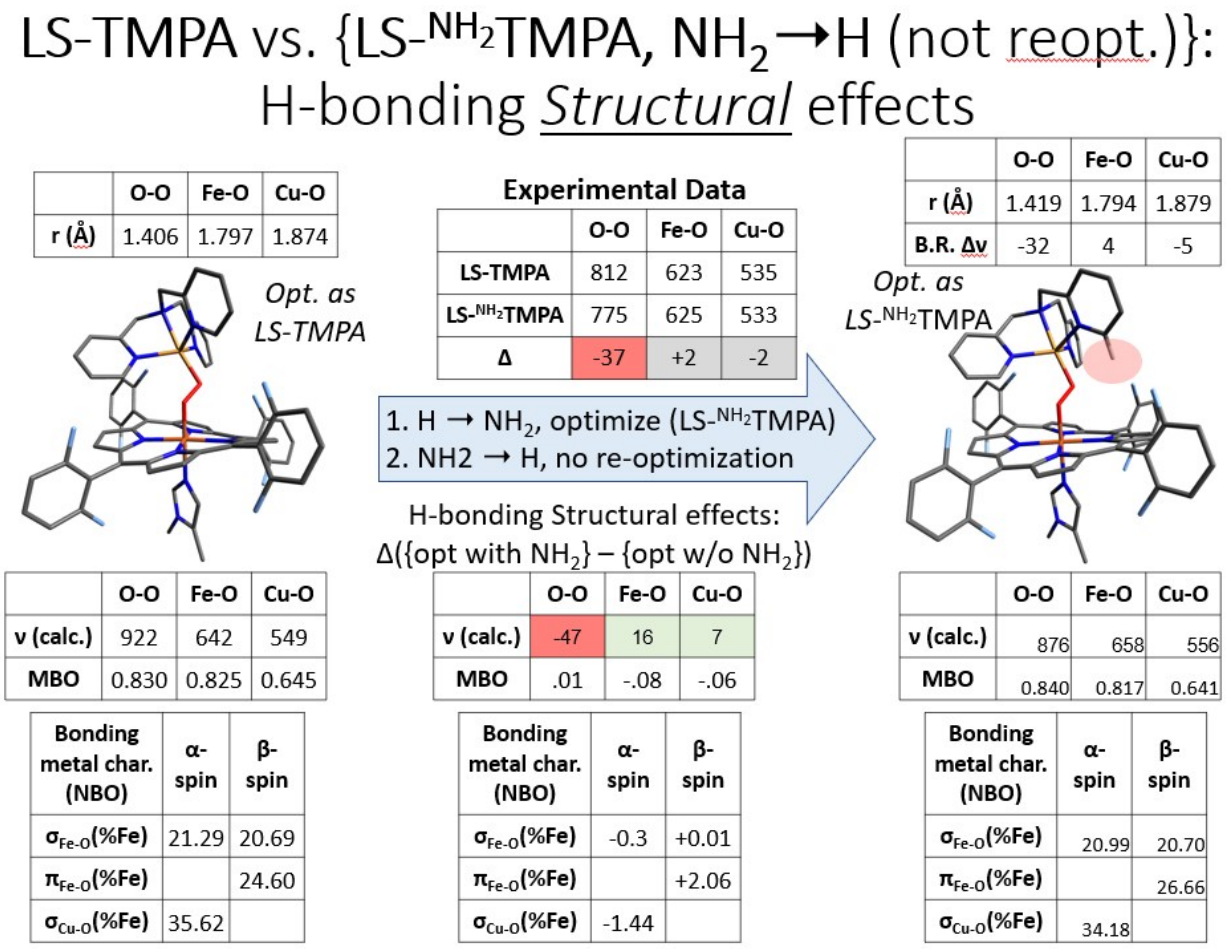


Figure S14. These DFT results are interpreted largely by the changes in metal character in the M-O bonds, which serve as a good probe of the bond strength. The results suggest that H-bonding causes a transfer of charge from metals to peroxo, yet the O-O bond order and ν(O-O) increase. This could be due to a decrease in electron repulsion, as explained for Cu/O_2 chemistry.[6,13] The Fe-O bond is impacted by net decrease in donation from O_2, especially β-spin (which derives from the O_2 π^*_v that interacts with the H-bond), therefore weakening it slightly. The Cu-O bond exhibits a substantial decrease in donation from O_2, therefore weakening the bond.



	O-O	Fe-O	Cu-O
r (Å)	1.406	1.797	1.874

	O-O	Fe-O	Cu-O
LS-TMPA	812	623	535
LS-^{NH_2}TMPA	775	625	533
Δ	-37	+2	-2

	O-O	Fe-O	Cu-O
r (Å)	1.419	1.794	1.879
B.R. Δν	-32	4	-5

	O-O	Fe-O	Cu-O
ν (calc.)	922	642	549
MBO	0.830	0.825	0.645

	O-O	Fe-O	Cu-O
ν (calc.)	-47	16	7
MBO	.01	-.08	-.06

	O-O	Fe-O	Cu-O
ν (calc.)	876	658	556
MBO	0.840	0.817	0.641

Bonding metal char. (NBO)	α-spin	β-spin
$\sigma_{Fe\text{-}O}$(%Fe)	21.29	20.69
$\pi_{Fe\text{-}O}$(%Fe)		24.60
$\sigma_{Cu\text{-}O}$(%Fe)	35.62	

Bonding metal char. (NBO)	α-spin	β-spin
$\sigma_{Fe\text{-}O}$(%Fe)	-0.3	+0.01
$\pi_{Fe\text{-}O}$(%Fe)		+2.06
$\sigma_{Cu\text{-}O}$(%Fe)	-1.44	

Bonding metal char. (NBO)	α-spin	β-spin
$\sigma_{Fe\text{-}O}$(%Fe)	20.99	20.70
$\pi_{Fe\text{-}O}$(%Fe)		26.66
$\sigma_{Cu\text{-}O}$(%Fe)	34.18	

Figure S15. The decrease in O-O bond stretching frequency correlates directly to the bond elongation, and matches reasonably well with the change predicted by Badger's Rule (shown in the table in the top-right). The changes in the Fe-O bond can be described as a decrease in α-spin σ donation due to the increased competition with donation into Cu (attributable to the wider dihedral angle). The β-spin donation (both σ and π) from O_2 to Fe increases due to the enhanced orbital overlap of the O_2 π^*_σ and π^*_v with the Fe dz^2 and dπ orbitals (attributable to both the wider dihedral and shorter Fe-O bond). The Cu-O bond weakens slightly due to the competition with Fe donation, as well as the Cu-O bond elongation.

Table S5. Selected bond lengths for the calculated DFT structures comparing **LS-TMPA**, **LS-^{PV}TMPA**, and **LS-^{A2}TMPA**.

	LS-TMPA	**LS-^{PV}TMPA**	**LS-^{A2}TMPA**
***r*(O–O), Å**	1.406	1.409	1.407
***r*(Fe–O), Å**	1.797	1.813	1.806
***r*(Cu–O, Å**	1.874	1.900	1.902

Cartesian Coordinates for calculated DFT structures

LS-TMPA

```
Fe 0.9421300000 -0.1470500000 0.5889800000
Cu -2.4915500000 0.0644600000 -1.8821300000
O -0.0157700000 -0.0163300000 -0.9256900000
O -1.1044500000 -0.8953400000 -1.0657100000
N 1.4031600000 -2.0244100000 0.1396700000
N -0.5518600000 -0.7852700000 1.7495400000
N 0.5380300000 1.7370400000 1.1407700000
C -2.3933600000 -0.8473400000 3.1543700000
C -1.8919300000 -2.1157800000 3.0953700000
C -0.7645400000 -2.0799800000 2.1803900000
C -1.5365600000 -0.0174900000 2.3248500000
C -1.6337500000 1.3759300000 2.2472700000
C -0.0792600000 -3.2053600000 1.7179600000
C 0.8806000000 -3.1657500000 0.7014700000
C 1.4172900000 -4.3346400000 0.0291500000
C 2.2424700000 -3.8787500000 -0.9585400000
C 2.2416900000 -2.4287900000 -0.8741000000
C 3.0545600000 -1.5904900000 -1.6455500000
C 3.2018500000 -0.2193600000 -1.4170800000
C 4.2157500000 0.6224300000 -2.0321000000
C 4.1385000000 1.8428100000 -1.4268500000
C 3.0382300000 1.7735300000 -0.4797900000
C 2.5506900000 2.8579200000 0.2542300000
C 1.3420800000 2.8417900000 0.9544700000
C 0.6811500000 4.0251400000 1.4719100000
```

C -0.5450900000 3.6293600000 1.9243900000
C -0.6160700000 2.1910700000 1.7471700000
C 3.8812500000 -2.2220400000 -2.7100500000
C 5.2573100000 -2.4255800000 -2.5737200000
C 3.3308000000 -2.6711900000 -3.9129700000
C 6.0516500000 -3.0150400000 -3.5489400000
C 4.0665100000 -3.2711700000 -4.9261800000
C 5.4429000000 -3.4395200000 -4.7355500000
C -0.4340100000 -4.5352300000 2.2814500000
C -1.6536300000 -5.1718200000 2.0364300000
C 0.4538500000 -5.2451800000 3.0959200000
C -1.9948100000 -6.4153600000 2.5519600000
C 0.1760400000 -6.4926600000 3.6395500000
C -1.0645300000 -7.0776600000 3.3611200000
C -2.8412500000 2.0181300000 2.8329800000
C -2.8325900000 2.6669300000 4.0711800000
C -4.0790900000 1.9971300000 2.1862300000
C -3.9499300000 3.2681500000 4.6369300000
C -5.2341800000 2.5742600000 2.6946900000
C -5.1600400000 3.2178200000 3.9356800000
C 3.3242900000 4.1297800000 0.2345600000
C 3.2697600000 5.0416700000 -0.8202700000
C 4.1625200000 4.4902100000 1.2927200000
C 3.9842500000 6.2320100000 -0.8537000000
C 4.9042500000 5.6644300000 1.3235000000
C 4.8106200000 6.5381800000 0.2340200000
N 2.4901500000 0.5122600000 -0.4915300000
F 4.2509600000 3.6154700000 2.3763800000
F 5.8580800000 -2.0146700000 -1.3834400000
F 1.6873700000 -4.6565800000 3.3773300000
F -1.6292400000 2.7016900000 4.7755500000
F -4.1547500000 1.3535600000 0.9404300000
F -2.5809300000 -4.5180700000 1.2197800000
F 2.4301200000 4.7364500000 -1.8974700000
F 1.9538600000 -2.5073500000 -4.1013900000
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H 6.0402200000 -3.9037200000 -5.5104900000
H 2.8142500000 -4.4589000000 -1.6655200000
H 1.1722800000 -5.3568100000 0.2708600000
H -2.2557200000 -2.9957500000 3.6011900000

H -3.2386300000 -0.4920500000 3.7224900000
H -1.3220900000 4.2422600000 2.3525600000
H 1.0904900000 5.0229400000 1.4505100000
H 4.7444400000 2.7155700000 -1.6123900000
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H 3.5738200000 -3.5938000000 -5.8338400000
H -2.9574100000 -6.8502600000 2.3177300000
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H -3.8708700000 3.7534400000 5.6006400000
H -6.1590600000 2.5205200000 2.1356800000
H -6.0453900000 3.6777200000 4.3568300000
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H 5.5361700000 5.8817200000 2.1743900000
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C 5.3686700000 -1.0034300000 3.9889300000
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H 3.3145300000 -0.6882500000 6.2284700000
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H 5.9948400000 -1.4115300000 3.1920500000
H 5.8854600000 -0.1316800000 4.4089200000
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N -1.8868000000 -0.2414000000 -3.8707900000
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H -3.4258900000 2.1856800000 -4.3322400000
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H 0.2651000000 -1.9349600000 -5.8253500000
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H -0.2026200000 -1.3442700000 -3.4274600000

LS-^{NH2}TMPA (O_{Cu}-bound via π^*_v)

Fe 1.0100800000 -0.0311400000 0.6728500000
Cu -2.5521200000 -0.0245000000 -1.7848000000
O -0.0369800000 -0.0433300000 -0.7839200000
O -1.2576800000 -0.7512200000 -0.6319100000
N 1.0744000000 -2.0275300000 0.6636400000
N -0.5090200000 -0.0747200000 1.9731700000
N 0.9777100000 1.9794400000 0.7335000000

C -2.3085600000 0.5398000000 3.2993600000
C -2.1030800000 -0.7952400000 3.4970200000
C -1.0061400000 -1.1830600000 2.6277100000
C -1.3081400000 0.9813800000 2.3436700000
C -1.1581200000 2.3056700000 1.9214600000
C -0.6408500000 -2.5049300000 2.3721100000
C 0.3014400000 -2.8851200000 1.4157800000
C 0.5944100000 -4.2593600000 1.0562600000
C 1.5434400000 -4.2182900000 0.0756800000
C 1.8434400000 -2.8175100000 -0.1628000000
C 2.8222300000 -2.3627500000 -1.0524400000
C 3.1782100000 -1.0214800000 -1.2080100000
C 4.3022000000 -0.5577700000 -2.0051200000
C 4.4121700000 0.7841300000 -1.7914900000
C 3.3360500000 1.1558200000 -0.8887400000
C 3.0675000000 2.4648600000 -0.4851300000
C 1.9266700000 2.8421100000 0.2257700000
C 1.5065700000 4.2158200000 0.4307900000
C 0.2713800000 4.1703300000 1.0093900000
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C 3.6354200000 -3.3853800000 -1.7693100000
C 4.9253600000 -3.7143300000 -1.3388100000
C 3.1893600000 -4.0938100000 -2.8851300000
C 5.7306100000 -4.6611400000 -1.9573600000
C 3.9381300000 -5.0554800000 -3.5494000000
C 5.2246500000 -5.3352400000 -3.0749300000
C -1.4018100000 -3.5769500000 3.0719100000
C -2.4613100000 -4.2509300000 2.4590200000
C -1.1287900000 -3.9598800000 4.3862700000
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C -4.3167000000 5.0815200000 2.9177900000
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C 3.8283700000 4.3712900000 -1.9776900000

C 5.2188900000 3.7385600000 -0.1794600000
C 4.7175400000 5.3657400000 -2.3637400000
C 6.1518200000 4.7120900000 -0.5134800000
C 5.8907800000 5.5308800000 -1.6182600000
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F 5.4203400000 -3.0471700000 -0.2169800000
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F -2.7823100000 -3.8994000000 1.1425400000
F 2.6587900000 4.1970800000 -2.7248200000
F 1.8973500000 -3.8202400000 -3.3664100000
H 6.6023300000 6.2974800000 -1.8991100000
H 5.8317100000 -6.0795900000 -3.5748600000
H 2.0116900000 -5.0486800000 -0.4288600000
H 0.1353800000 -5.1282300000 1.5004400000
H -2.6519400000 -1.4654500000 4.1395100000
H -3.0489000000 1.1751100000 3.7595300000
H -0.3625500000 4.9984900000 1.2823800000
H 2.0713500000 5.0872100000 0.1397100000
H 5.1311800000 1.4686100000 -2.2131100000
H 4.9192500000 -1.1828700000 -2.6307300000
H 6.7198700000 -4.8644900000 -1.5694600000
H 3.5261500000 -5.5637600000 -4.4110700000
H -4.0189500000 -5.7228600000 2.5474700000
H -1.5762300000 -5.1897500000 6.0857800000
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H 1.3154300000 1.2349500000 3.6434400000
N 3.2569100000 0.4459400000 4.1682100000
C 4.1536500000 -0.3837200000 3.4871100000
H 3.9198800000 -1.2705600000 1.4704500000

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H 2.5941900000 1.6331400000 5.7514200000
H 5.3450800000 -1.3558000000 4.9965600000
H 5.9859300000 -1.4482200000 3.3493500000
H 6.1122200000 0.0606200000 4.2646700000
N -2.0324200000 1.9797100000 -2.1251400000
N -4.1552700000 0.5796900000 -2.9878700000
N -2.1774200000 -1.2037700000 -3.5314700000
N -4.0990400000 -0.6952500000 -0.6206500000
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C -0.8145500000 2.5493800000 -2.0451200000
C -3.7314800000 0.4452700000 -4.4069100000
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C -3.9787200000 -1.0275600000 0.6746600000
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H -5.0942100000 2.4824900000 -3.3072300000
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H -3.3538600000 -1.0465700000 -6.6989600000

C -6.3643500000 -1.2049300000 0.8975800000
H -7.4549200000 -0.7748900000 -0.9264300000
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N -0.7162400000 -2.7002400000 -2.5071400000
H -0.7847800000 -2.0798800000 -1.6861200000
H 0.1374100000 -3.2285400000 -2.6201600000

LS-^{NH2}TMPA (O_{Cu}-bound via π^*_σ)

Fe 0.8343900000 -0.2831100000 0.7814700000
Cu -2.1534200000 0.5266300000 -2.2737700000
O -0.1830500000 0.3605400000 -0.5481000000
O -1.0326300000 -0.5588800000 -1.2168500000
N 1.4000100000 -1.9028800000 -0.2427800000
N -0.6431200000 -1.3435000000 1.6243500000
N 0.3287900000 1.3146200000 1.9027900000
C -2.5036100000 -1.9390100000 2.8730700000
C -1.9642100000 -3.0936100000 2.3817600000
C -0.8208400000 -2.7125700000 1.5749700000
C -1.6557000000 -0.8530700000 2.4193800000
C -1.7773100000 0.4636900000 2.8690400000
C -0.0646600000 -3.5960800000 0.8041700000
C 0.9329900000 -3.1902300000 -0.0841500000
C 1.6181100000 -4.0837000000 -0.9998300000
C 2.4972600000 -3.3221300000 -1.7106700000
C 2.3674200000 -1.9608100000 -1.2207800000
C 3.1724800000 -0.8976400000 -1.6415500000
C 3.1560600000 0.3753300000 -1.0652800000
C 4.0157700000 1.4727300000 -1.4740500000
C 3.7395500000 2.5211800000 -0.6480300000
C 2.6990900000 2.0773200000 0.2631600000
C 2.1090000000 2.8895800000 1.2345200000
C 1.0023500000 2.5149100000 1.9989800000
C 0.3093000000 3.3988000000 2.9193400000
C -0.8174200000 2.7454800000 3.3239700000
C -0.7991900000 1.4412300000 2.6882900000

C 4.1592600000 -1.1633200000 -2.7226800000
C 5.5355700000 -1.2067200000 -2.4782800000
C 3.7830200000 -1.4076200000 -4.0464900000
C 6.4874600000 -1.4529500000 -3.4590000000
C 4.6834000000 -1.6620200000 -5.0728200000
C 6.0494000000 -1.6812400000 -4.7686800000
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C -1.4721200000 -5.6928800000 0.4506300000
C 0.5890700000 -5.8987000000 1.5731400000
C -1.7183100000 -7.0534100000 0.5721100000
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C -0.7612600000 -7.8442100000 1.2180400000
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C -3.0527500000 0.9699200000 5.0029200000
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C -4.1954900000 1.3220200000 5.7100100000
C -5.3986200000 1.4184300000 3.5999800000
C -5.3769800000 1.5468700000 4.9938700000
C 2.6282000000 4.2749000000 1.3908800000
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C 3.8753700000 4.5488100000 1.9584800000
C 2.3649600000 6.7002400000 1.0872200000
C 4.3920300000 5.8299100000 2.1059500000
C 3.6224400000 6.9122700000 1.6646900000
N 2.3580100000 0.7715600000 -0.0119700000
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F 5.9687500000 -0.9969200000 -1.1683900000
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F 0.6567100000 5.1818700000 0.3784900000
F 2.4189000000 -1.3907100000 -4.3498700000
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H 6.7720100000 -1.8774600000 -5.5510300000
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H -6.3002400000 1.5877900000 3.0263500000
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H 5.3655000000 5.9697800000 2.5568200000
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C 3.4035400000 -1.2536600000 2.1439900000
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N 2.8003600000 -1.5458600000 4.2497600000
C 3.8815400000 -1.6631700000 3.3704400000
H 3.9251900000 -1.1943200000 1.2042600000
C 2.8144600000 -1.8670600000 5.6761400000
C 5.2238100000 -2.1474300000 3.7976200000
H 3.5543900000 -1.2546300000 6.1969800000
H 3.0516500000 -2.9230600000 5.8264800000
H 1.8281300000 -1.6621800000 6.0930400000
H 5.1812500000 -3.1669700000 4.2003300000
H 5.9030300000 -2.1538100000 2.9419000000
H 5.6637800000 -1.5053900000 4.5706200000
N -2.7311900000 2.2621500000 -1.0972900000
N -3.4055600000 1.5472300000 -3.6015400000
N -0.7038900000 1.3383700000 -3.4959700000
N -3.6132800000 -0.9022600000 -2.5263000000
C -3.8303400000 2.8734200000 -1.5903900000
C -2.0669800000 2.8267200000 -0.0736600000
C -2.6219100000 2.5647900000 -4.3529900000
C -3.9322800000 0.4781300000 -4.4884900000
C -4.4713900000 2.1760500000 -2.7714300000
C 0.6085000000 1.0388600000 -3.4375400000
C -1.1562800000 2.1917600000 -4.4385500000
C -4.3381700000 -0.7230100000 -3.6625200000

C -3.8862200000 -1.9601500000 -1.7156500000
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C -2.4878400000 4.0222700000 0.5149900000
H -3.0497400000 2.7291100000 -5.3492000000
H -2.7017200000 3.5120400000 -3.8089800000
H -4.7693100000 0.8399200000 -5.0986000000
H -3.1188500000 0.1999000000 -5.1695000000
H -5.1278300000 1.3744100000 -2.4180600000
H -5.0786400000 2.8694900000 -3.3658200000
C 1.5285900000 1.5945500000 -4.3256200000
C -0.2976400000 2.7655500000 -5.3788600000
C -5.3505500000 -1.5848200000 -4.0511200000
C -4.8928900000 -2.8963900000 -2.0742300000
H -5.2028200000 4.5304900000 -1.4725500000
C -3.6388900000 4.6433500000 0.0248300000
H -1.9126700000 4.4501600000 1.3241800000
H 2.5772500000 1.3456500000 -4.2402200000
H -0.6884500000 3.4388800000 -6.1326300000
C 1.0664100000 2.4659700000 -5.3166500000
H -5.9138000000 -1.4003400000 -4.9568200000
C -5.6153500000 -2.7039400000 -3.2365000000
H -5.0841800000 -3.7390200000 -1.4207900000
H -3.9928900000 5.5717100000 0.4584400000
H 1.7546100000 2.9057900000 -6.0291400000
H -6.3909400000 -3.4078000000 -3.5164800000
H -1.1836100000 2.2937400000 0.2511400000
H 0.8972600000 0.3564900000 -2.6512200000
N -3.2044200000 -2.0537100000 -0.5417000000
H -3.1752800000 -2.9673100000 -0.1113900000
H -2.3311400000 -1.5095500000 -0.4817600000

LS-^{NH2}TMPA (O_{Fe}-bound via π^*_v)

Fe 0.9757000000 0.1691700000 -0.6901700000
Cu -2.5177900000 -0.2644800000 1.8079000000
O -0.0468700000 -0.0866500000 0.7805900000
O -1.2259500000 0.6942200000 0.8585200000
N -0.5816600000 0.5580800000 -1.8865800000
N 0.8342400000 -1.7936400000 -1.1364100000

N 2.5656900000 -0.2385500000 0.4799900000
C 1.2397700000 -4.0708800000 -1.3021400000
C 0.0293000000 -3.8348300000 -1.8852000000
C -0.2115700000 -2.4065200000 -1.7983300000
C 1.7167100000 -2.7982500000 -0.7956300000
C 2.8433600000 -2.6466500000 0.0153300000
C -1.3140800000 -1.7547400000 -2.3533100000
C -1.4294900000 -0.3656600000 -2.4509900000
C -2.4492200000 0.3073800000 -3.2373000000
C -2.1980900000 1.6451300000 -3.1479100000
C -1.0546000000 1.7966900000 -2.2667700000
C -0.5898400000 3.0223100000 -1.7906600000
C 0.4104600000 3.1547600000 -0.8277600000
C 0.8338900000 4.4198800000 -0.2592000000
C 1.8183800000 4.1378300000 0.6414600000
C 2.0118000000 2.6982900000 0.6196700000
C 2.9759700000 2.0269900000 1.3786700000
C 3.2226400000 0.6542500000 1.3012500000
C 4.2684400000 -0.0320200000 2.0413600000
C 4.2579600000 -1.3319000000 1.6306300000
C 3.1868000000 -1.4557600000 0.6584500000
C -1.2304700000 4.2573100000 -2.3196400000
C -0.8874900000 4.7884600000 -3.5647500000
C -2.2182000000 4.9550900000 -1.6217500000
C -1.4693500000 5.9279300000 -4.1048500000
C -2.8397100000 6.1000400000 -2.1035500000
C -2.4549500000 6.5854100000 -3.3590400000
C -2.4380200000 -2.5742500000 -2.8828600000
C -3.6785100000 -2.6190100000 -2.2376600000
C -2.3513400000 -3.3395400000 -4.0492500000
C -4.7593200000 -3.3676200000 -2.6814400000
C -3.3937300000 -4.1115100000 -4.5471100000
C -4.6073300000 -4.1219500000 -3.8509000000
C 3.7410000000 -3.8193300000 0.2023200000
C 4.9344400000 -3.9385000000 -0.5145500000
C 3.4709100000 -4.8645000000 1.0863600000
C 5.8134200000 -5.0047300000 -0.3852300000
C 4.3039700000 -5.9617500000 1.2633600000
C 5.4862100000 -6.0245900000 0.5166800000
C 3.8549400000 2.8408300000 2.2662900000

C 3.4213600000 3.4186000000 3.4611000000
C 5.1948700000 3.0896200000 1.9481400000
C 4.2224200000 4.1805700000 4.2994300000
C 6.0534700000 3.8394500000 2.7414600000
C 5.5559500000 4.3879700000 3.9287200000
N 1.1433000000 2.1222700000 -0.2821100000
F 5.6889800000 2.5530100000 0.7598200000
F 0.0967300000 4.1243900000 -4.3020900000
F -1.1460300000 -3.3204300000 -4.7496400000
F 5.2519200000 -2.9141800000 -1.4159800000
F 2.2913900000 -4.7943200000 1.8332500000
F -3.8379100000 -1.8661400000 -1.0633500000
F 2.0817400000 3.2177500000 3.8404500000
F -2.6026200000 4.4601700000 -0.3732700000
H 6.2053600000 4.9774800000 4.5637200000
H -2.9238700000 7.4768500000 -3.7568400000
H -2.7413600000 2.4577500000 -3.6038600000
H -3.2287900000 -0.1875400000 -3.7943500000
H -0.6357500000 -4.5515500000 -2.3381800000
H 1.7497900000 -5.0143800000 -1.1892400000
H 4.8925500000 -2.1396200000 1.9593500000
H 4.9160900000 0.4276200000 2.7706300000
H 2.3752500000 4.8297500000 1.2528300000
H 0.4280200000 5.3841000000 -0.5208000000
H -1.1562200000 6.2869600000 -5.0761700000
H -3.5996000000 6.5921300000 -1.5111300000
H -5.6886500000 -3.3571900000 -2.1273300000
H -3.2549600000 -4.6796000000 -5.4573400000
H -5.4346700000 -4.7152500000 -4.2199500000
H 6.7211900000 -5.0334800000 -0.9730100000
H 4.0342400000 -6.7367100000 1.9684000000
H 6.1536800000 -6.8687100000 0.6376800000
H 3.8131600000 4.5948400000 5.2112500000
H 7.0786500000 3.9902100000 2.4304700000
N 2.2373400000 0.4250400000 -2.2590900000
C 3.3215900000 -0.3103000000 -2.5009000000
C 2.1630800000 1.3794300000 -3.2693200000
H 3.6851200000 -1.1369600000 -1.9186800000
N 3.9488400000 0.1303100000 -3.6296100000
C 3.2217700000 1.2143100000 -4.1346300000

H 1.3783000000 2.1125300000 -3.3175600000
C 5.1690600000 -0.4410200000 -4.1994700000
C 3.6141400000 1.9571800000 -5.3645400000
H 5.9682900000 0.3038800000 -4.2136600000
H 4.9847200000 -0.7910300000 -5.2179000000
H 5.4780600000 -1.2851100000 -3.5819800000
H 3.6331100000 1.3067800000 -6.2477200000
H 2.8953700000 2.7583800000 -5.5532500000
H 4.6078600000 2.4118300000 -5.2687300000
N -1.7377200000 -0.0828900000 3.8710200000
N -4.1700700000 -1.0402900000 2.8567500000
N -3.9873100000 0.8702100000 0.9720400000
N -2.1885900000 -2.3413800000 1.5731600000
C -2.7468600000 -0.3342600000 4.7460600000
C -0.7134300000 0.7175600000 4.2618000000
C -5.2438200000 -0.0137700000 2.8274800000
C -4.5459900000 -2.2638200000 2.0953500000
C -3.7563800000 -1.3492200000 4.2557700000
C -3.8336000000 1.5678700000 -0.1668500000
C -5.2181500000 0.7240600000 1.5111600000
C -3.2988800000 -3.0725600000 1.8217700000
C -1.0184900000 -2.9714100000 1.3687900000
C -2.8265900000 0.2484200000 6.0016900000
C -0.7367700000 1.3638800000 5.5297100000
H -6.2275300000 -0.4573300000 3.0240900000
H -5.0305000000 0.6951900000 3.6362000000
H -5.2952300000 -2.8550000000 2.6359300000
H -4.9866100000 -1.9381000000 1.1470000000
H -3.2840400000 -2.3362600000 4.2463400000
H -4.6278000000 -1.4025800000 4.9183000000
C -4.9183200000 2.1497100000 -0.8232800000
C -0.9110100000 -4.3646300000 1.3922700000
C -6.3505800000 1.2642600000 0.9040000000
C -3.2763400000 -4.4664400000 1.8430400000
H -2.8186500000 1.6415900000 -0.5270700000
C -1.7965200000 1.1324400000 6.3854000000
H -0.1716200000 -2.3244100000 1.1816600000
H -3.6552800000 0.0274800000 6.6625400000
H 0.0812900000 2.0196800000 5.8043300000
C -6.1968400000 1.9901200000 -0.2832300000

H -4.7578400000 2.7034200000 -1.7387000000
C -2.0609500000 -5.1233500000 1.6200200000
H -7.3269200000 1.1204800000 1.3506600000
H -4.1841500000 -5.0214900000 2.0485400000
H 0.0532800000 -4.8285000000 1.2441800000
H -1.8316800000 1.6217200000 7.3524700000
H -7.0616800000 2.4194200000 -0.7756300000
H -2.0129200000 -6.2060500000 1.6424200000
N 0.3608200000 0.8353500000 3.4314000000
H 0.9693600000 1.6306900000 3.5678400000
H 0.2722200000 0.5006900000 2.4679700000

LS-^{NH2}TMPA (O_{Fe}-bound via π^*_σ)

Fe -0.8768400000 -0.4203300000 -0.6595200000
Cu 2.2229000000 0.4437400000 2.0896300000
O -0.0856200000 0.1364700000 0.8621300000
O 0.8586300000 -0.7063200000 1.4918000000
N 0.6781600000 -1.4608400000 -1.3604900000
N -0.2316500000 1.2235300000 -1.6234800000
N -2.4783000000 0.6252400000 -0.0430800000
C -0.0166900000 3.3931600000 -2.4109400000
C 1.1762200000 2.7675900000 -2.6289300000
C 1.0255400000 1.3991700000 -2.1678900000
C -0.8884300000 2.4261300000 -1.7703100000
C -2.1851100000 2.7040500000 -1.3268300000
C 1.9614600000 0.3869900000 -2.3810600000
C 1.7362500000 -0.9613000000 -2.0835900000
C 2.5757700000 -2.0502600000 -2.5512800000
C 2.0026600000 -3.2094600000 -2.1133400000
C 0.8387300000 -2.8329200000 -1.3328200000
C 0.0732400000 -3.7150500000 -0.5678500000
C -0.9660100000 -3.3040200000 0.2721600000
C -1.6023800000 -4.1452200000 1.2681800000
C -2.5177900000 -3.3669500000 1.9150800000
C -2.4769300000 -2.0569700000 1.2887900000
C -3.3437500000 -1.0051900000 1.5969900000
C -3.3814800000 0.2111700000 0.9102300000
C -4.4257700000 1.2097100000 1.0662900000

C -4.1513400000 2.2135600000 0.1826100000
C -2.9095200000 1.8584400000 -0.4821900000
C 0.3851800000 -5.1673900000 -0.6224400000
C -0.4881700000 -6.0777500000 -1.2265000000
C 1.5451900000 -5.7277400000 -0.0820200000
C -0.2523200000 -7.4436500000 -1.3031400000
C 1.8430000000 -7.0834200000 -0.1268900000
C 0.9296200000 -7.9448300000 -0.7452700000
C 3.2444900000 0.7448200000 -3.0461600000
C 4.4548800000 0.7980600000 -2.3527100000
C 3.3302100000 1.0445400000 -4.4089600000
C 5.6731200000 1.1224100000 -2.9325100000
C 4.5148600000 1.3796400000 -5.0527700000
C 5.6948300000 1.4161000000 -4.3010400000
C -2.7947600000 3.9955400000 -1.7419500000
C -3.2841800000 4.1887000000 -3.0372700000
C -2.9144100000 5.0992100000 -0.8966400000
C -3.8554300000 5.3733500000 -3.4810700000
C -3.4754200000 6.3118100000 -1.2702900000
C -3.9502400000 6.4415400000 -2.5810900000
C -4.3143500000 -1.1998600000 2.7088800000
C -4.1455100000 -0.5793900000 3.9490600000
C -5.4481100000 -2.0085000000 2.5969500000
C -5.0199200000 -0.7284000000 5.0167800000
C -6.3608600000 -2.2032300000 3.6261400000
C -6.1382600000 -1.5528800000 4.8452700000
N -1.5180600000 -2.0440400000 0.2996000000
F -5.6684700000 -2.6496600000 1.3788100000
F -1.6643000000 -5.5737400000 -1.7900600000
F 2.1552700000 0.9986400000 -5.1577200000
F -3.1848500000 3.1177300000 -3.9334000000
F -2.4216700000 4.9693500000 0.4151300000
F 4.4299300000 0.5124300000 -0.9792600000
F -3.0220000000 0.2400300000 4.1185200000
F 2.4524600000 -4.8708300000 0.5462100000
H -6.8364800000 -1.6881500000 5.6619800000
H 1.1379900000 -9.0064900000 -0.7915600000
H 2.3392500000 -4.2203900000 -2.2790600000
H 3.4668900000 -1.9329300000 -3.1474500000
H 2.0710700000 3.1807300000 -3.0662200000

H -0.2803900000 4.4160900000 -2.6278800000
H -4.7154200000 3.1159300000 0.0070100000
H -5.2617900000 1.1310800000 1.7432700000
H -3.1668200000 -3.6455500000 2.7298400000
H -1.3548500000 -5.1778700000 1.4571500000
H -0.9719400000 -8.0894800000 -1.7883600000
H 2.7596500000 -7.4488400000 0.3166700000
H 6.5714100000 1.1460100000 -2.3298600000
H 4.5083900000 1.5989900000 -6.1121700000
H 6.6307600000 1.6732400000 -4.7813000000
H -4.2156300000 5.4524900000 -4.4980800000
H -3.5344700000 7.1259900000 -0.5602600000
H -4.3929200000 7.3762500000 -2.9016700000
H -4.8265200000 -0.2177300000 5.9508500000
H -7.2198900000 -2.8423400000 3.4708000000
N -1.9328700000 -0.9741600000 -2.3156300000
C -2.4606200000 -0.1427200000 -3.2125300000
C -2.2749800000 -2.2634000000 -2.7121000000
H -2.3954700000 0.9294000000 -3.2151600000
N -3.1328400000 -0.8449300000 -4.1712400000
C -3.0221600000 -2.2061200000 -3.8677000000
H -1.9790900000 -3.1360500000 -2.1596300000
C -3.8377300000 -0.2614200000 -5.3124800000
C -3.6334100000 -3.2810100000 -4.6980800000
H -4.8761100000 -0.6002900000 -5.3279100000
H -3.3527500000 -0.5456900000 -6.2498400000
H -3.8196200000 0.8244900000 -5.2134500000
H -3.2581800000 -3.2658300000 -5.7286900000
H -3.3937700000 -4.2563000000 -4.2671600000
H -4.7259600000 -3.1925800000 -4.7439100000
N 1.3837800000 1.0578200000 3.8523000000
N 3.8707400000 1.5338800000 2.8056000000
N 3.6821200000 -0.8577400000 1.5898500000
N 1.9424400000 2.6523500000 1.3167100000
C 2.1517900000 1.8781600000 4.5968400000
C 0.1623800000 0.6935400000 4.2916000000
C 4.9018600000 0.5222300000 3.1509900000
C 4.3133300000 2.3836800000 1.6594400000
C 3.4633900000 2.3459900000 3.9891700000
C 3.5372500000 -1.8931900000 0.7446500000

C 4.8924800000 -0.5944900000 2.1326300000
C 3.1546500000 3.2414600000 1.2016900000
C 0.8326100000 3.4025100000 1.1092200000
C 1.7212100000 2.3428200000 5.8437000000
C -0.3431300000 1.1379300000 5.5119700000
H 5.8964900000 0.9777600000 3.2384700000
H 4.6371800000 0.1100200000 4.1319800000
H 5.1682700000 3.0087800000 1.9478700000
H 4.6368700000 1.7117600000 0.8599400000
H 3.3352800000 3.3827900000 3.6634500000
H 4.2579800000 2.3489900000 4.7438000000
C 4.6151500000 -2.7040100000 0.3877200000
C 0.9279400000 4.7453300000 0.6569900000
C 6.0175400000 -1.3495100000 1.8080400000
C 3.3298700000 4.5544000000 0.7801400000
H 2.5351500000 -2.0480100000 0.3732000000
C 0.4564900000 1.9693300000 6.3049200000
H 2.3600300000 2.9915900000 6.4316600000
H -1.3372300000 0.8432200000 5.8194600000
H 4.4560600000 -3.5335300000 -0.2859800000
C 5.8752800000 -2.4214800000 0.9191500000
H 6.9790200000 -1.1085700000 2.2456000000
C 2.1795800000 5.3066000000 0.4770200000
H 4.3209400000 4.9862600000 0.7145100000
H 0.0200800000 5.3052800000 0.4720600000
H 0.0987000000 2.3256700000 7.2640200000
H 6.7348800000 -3.0250100000 0.6514300000
H 2.2729000000 6.3302700000 0.1310800000
H -0.4035500000 0.0478400000 3.6307500000
N -0.3745300000 2.8408200000 1.4279300000
H -0.4028100000 1.8175500000 1.3618900000
H -1.1870600000 3.3153000000 1.0592300000

LS-^{2NH_2}TMPA (O_{Cu},O_{Cu}-bound)

Fe -1.0043000000 -0.0420400000 0.5771900000
Cu 2.8647400000 0.1237900000 -1.7672700000
O 0.3194600000 -0.1863700000 -0.6661700000
O 1.4118700000 0.7393500000 -0.6695400000

N -1.4273700000 1.8821700000 0.1667500000
N 0.1825300000 0.5490500000 2.0909500000
N -0.7002700000 -1.9765800000 1.0819000000
C 1.6037500000 0.5294600000 3.9245000000
C 1.1879600000 1.8165800000 3.7549800000
C 0.3183900000 1.8283500000 2.5944400000
C 0.9530500000 -0.2616300000 2.8976400000
C 1.0069100000 -1.6597700000 2.8442600000
C -0.2623400000 2.9823300000 2.0558900000
C -1.0413400000 2.9918300000 0.8925500000
C -1.5905600000 4.1923800000 0.2954100000
C -2.3305400000 3.7979600000 -0.7784900000
C -2.2372200000 2.3517100000 -0.8482500000
C -2.9294900000 1.5662800000 -1.7815800000
C -2.9127300000 0.1649400000 -1.7951200000
C -3.6482600000 -0.6482700000 -2.7478900000
C -3.4795500000 -1.9456800000 -2.3734900000
C -2.6315900000 -1.9368200000 -1.1949800000
C -2.2439800000 -3.0881700000 -0.5000000000
C -1.3337600000 -3.0878700000 0.5639700000
C -0.8581500000 -4.2851800000 1.2306600000
C 0.0970000000 -3.8913000000 2.1194800000
C 0.1861000000 -2.4464900000 2.0291200000
C -3.8612900000 2.2559500000 -2.7268300000
C -5.2507100000 2.1966600000 -2.5468500000
C -3.4548500000 3.0110600000 -3.8301300000
C -6.1728100000 2.8120600000 -3.3837600000
C -4.3193600000 3.6550400000 -4.7054200000
C -5.6955700000 3.5466300000 -4.4754600000
C -0.0775800000 4.2757300000 2.7819700000
C 1.1215600000 4.9941900000 2.8061800000
C -1.1234200000 4.8632100000 3.5066400000
C 1.3014500000 6.1974900000 3.4760800000
C -1.0131700000 6.0639900000 4.1971300000
C 0.2153700000 6.7341800000 4.1771800000
C 1.9430500000 -2.3585100000 3.7759000000
C 1.5586900000 -2.7775700000 5.0533700000
C 3.2681400000 -2.6406500000 3.4316400000
C 2.4049700000 -3.4300400000 5.9419700000
C 4.1662000000 -3.2878000000 4.2719900000

C 3.7215100000 -3.6848500000 5.5389000000
C -2.8231400000 -4.3947300000 -0.9340000000
C -2.0932000000 -5.3548700000 -1.6427900000
C -4.1497300000 -4.7470000000 -0.6586000000
C -2.6118900000 -6.5757000000 -2.0573100000
C -4.7295600000 -5.9493200000 -1.0459300000
C -3.9462500000 -6.8692600000 -1.7525500000
N -2.2796000000 -0.6434700000 -0.8745800000
F -4.9308300000 -3.8335200000 0.0501200000
F -5.7334900000 1.4777400000 -1.4507500000
F -2.3483000000 4.1951500000 3.5360800000
F 0.2448000000 -2.5173400000 5.4499200000
F 3.7144300000 -2.2369700000 2.1669200000
F 2.2194200000 4.4646800000 2.1073700000
F -0.7613800000 -5.0634600000 -1.9525600000
F -2.0740600000 3.1434800000 -4.0669900000
H -4.3751000000 -7.8136400000 -2.0654800000
H -6.3937300000 4.0371200000 -5.1427000000
H -2.8985600000 4.4207100000 -1.4515100000
H -1.4292600000 5.1968000000 0.6533300000
H 1.4425900000 2.6766000000 4.3544800000
H 2.2648700000 0.1421400000 4.6838100000
H 0.6784500000 -4.5107100000 2.7841600000
H -1.2070700000 -5.2870800000 1.0363600000
H -3.8769500000 -2.8289200000 -2.8480400000
H -4.2116400000 -0.2695700000 -3.5861300000
H -7.2313100000 2.7198900000 -3.1779700000
H -3.9237100000 4.2200000000 -5.5395000000
H 2.2609200000 6.6972700000 3.4428100000
H -1.8667800000 6.4550300000 4.7354700000
H 0.3268100000 7.6721900000 4.7073900000
H 2.0403000000 -3.7259600000 6.9170700000
H 5.1797800000 -3.4727700000 3.9404600000
H 4.4017600000 -4.1913200000 6.2130400000
H -1.9868000000 -7.2687300000 -2.6053800000
H -5.7625700000 -6.1539100000 -0.7959800000
N -2.6023200000 -0.0283400000 1.9004900000
C -2.5638800000 -0.4116700000 3.1739000000
C -3.9109300000 0.3603600000 1.6438600000
H -1.7037900000 -0.7826600000 3.7050100000

N -3.7968600000 -0.2867700000 3.7507000000
C -4.6729600000 0.2098800000 2.7823200000
H -4.2285600000 0.7163900000 0.6787700000
C -4.1334800000 -0.6181800000 5.1367500000
C -6.1161000000 0.4820500000 3.0443700000
H -4.9040900000 -1.3925700000 5.1677200000
H -4.4933400000 0.2682000000 5.6653000000
H -3.2392500000 -0.9900700000 5.6379300000
H -6.2564800000 1.2325400000 3.8324500000
H -6.5904000000 0.8606600000 2.1355000000
H -6.6562500000 -0.4225000000 3.3507800000
N 3.0087900000 -1.9644600000 -1.4416500000
N 4.5012900000 -0.3480200000 -2.9926300000
N 2.1527600000 0.7672300000 -3.7068600000
N 4.3747400000 1.4174400000 -0.9340100000
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LS-^{2NH_2}TMPA (O_{Cu},O_{Fe}-bound)

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