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Supporting Information

Hydrogen Bonds Dictate the Coordination Geometry of Copper: Characterization of a Square-Planar Copper(I) Complex

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Experimental Details

General Considerations: All commercially-available reagents were used as received without further purification. Benzyl potassium[1] and 6,6”-dihydroxyterpyridine (dhtp)[2] were prepared according to the literature. All manipulations were carried out under an atmosphere of nitrogen in an Innovative Technologies Pure LabHE GP-1 glovebox or using Shlenk techniques, unless otherwise specified. Degassed, anhydrous solvents were obtained by a SG Water USA solvent purification system or by drying overnight with CaH$_2$ followed by distillation. NMR spectra were collected on a Varian MR400 and were referenced to residual solvent peaks. IR spectra were collected on a Nicolet is10 spectrometer as KBr pellets, a diamond attenuated total reflectance (ATR) accessory, or as a solution in CH$_2$Cl$_2$ between KBr plates. EPR spectra were collected on a Bruker EMX EPR spectrometer. Electronic absorption spectra were collected on a Varian Cary-50 spectrophotometer. Near-infrared spectroscopic data was obtained on a Varian Cary-5000 spectrophotometer. X-ray photoelectron spectra were recorded on a Kratos Axis Ultra XPS (8 mA, 14 keV, Monochromatic Al) and referenced to C1s at 284.8 eV. Powder samples for XPS were prepared as a thin layer on double-sided carbon tape and mounted a glass slide. Voltammetry experiments were conducted using a Pine WaveNow potentiostat under N$_2$ in a cell consisting of a glassy carbon working electrode, platinum counter electrode and a silver wire reference electrode. All voltammetry experiments were referenced to SCE via an internal ferrocene reference introduced at the end of the experiment (Fc/Fc$^+$ = 0.46V vs SCE in CH_2Cl_2)[3] Elemental analyses were performed by Midwest Microlabs, LLC, Indianapolis, IN.

Synthesis of 6,6"-bis(2,4,6-trimethylanilido)terpyridine (H_2Tpy^{NMes}): 10 mL of THF was added to 600.0 mg (4.608 mmol) of benzyl potassium to form a dark red solution. 0.776 mL (5.530 mmol) of 2,4,6-trimethylaniline was then added to the solution causing a loss of color to yield a light red solution. This solution was stirred for 1 min then added to a slurry of 360.4 mg (0.922 mmol) and 6,6"-dibromoterpyridine in 10 mL THF. The solution was stirred at room temperature for 1 hour then quenched with a solution of saturated ammonium chloride. The organic layer was removed and the aqueous phase was washed with CH_2Cl_2. The organic phase was dried over $MgSO_4$, filtered and solvent was removed via rotary evaporation. Methanol was added to the resulting crude oil to precipitate a yellow solid, which was collected on a glass frit and washed with a minimal amount of methanol followed by pentane. The yellow solid was further purified by dissolving in dichloromethane and passage through a plug of basic alumina (4 x 3 cm). The CH_2Cl_2 was removed *in vacuo* to isolate 325 mg (70% yield) of an off-white powder. If desired, a crystalline sample can be obtained by recrystallization from hot toluene. Elemental analysis was obtained from this sample. ^1H NMR (700 MHz, $CDCl_3$) δ: 8.36 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 7.4 Hz, 2H), 7.91 (t, *J* = 7.8 Hz, H), 7.53 (dd, *J* = 7.4, 8.2 Hz, 2H), 6.98 (s, 4H), 6.08 (s, 2H), 6.05 (d, *J* = 8.2 Hz, 2H), 2.33 (s, 6H), 2.24 (s, 12H). ^{13}C NMR (175 MHz, $CDCl_3$) δ: 157.7, 155.8, 155.3, 138.7, 137.6, 136.8, 136.5, 134.1, 129.4, 120.7, 111.4, 105.9, 21.1, 18.6. IR (CH_2Cl_2, cm^{-1}): 3406 (N-H). Anal. calcd for C33H33N5: C, 79.33; H, 6.66; N, 14.02. Found: C, 79.45; H, 6.85; N, 13.74.

Synthesis of Cu(H_2Tpy^{NMes})Cl (1): 80.8 mg (0.162 mmol) of H_2Tpy^{NMes} in 10 mL of benzene was added to a vial containing 15.2 mg (0.154 mmol) copper(I) chloride. The solution was stirred at room temperature for 18 hrs, then the solvent was removed *in vacuo*. The crude black solid was collected on a sintered glass frit and washed with MeCN (3 x 2 mL) followed by diethyl ether (3 x 2 mL). The solid was washed through the frit with minimal CH_2Cl_2. The CH_2Cl_2 was concentrated and layered with diethyl ether and placed in a -33°C freezer overnight. The product precipitates as microcrystalline purple needles. The supernatant was decanted and the precipitate was dried under vacuum affording a 77.1mg (84%) yield. Crystals suitable for X-ray were grown from pentane diffusion into a concentrated toluene solution of **1** at 3°C. ^1H NMR (700 MHz, CD_2Cl_2) δ: 8.90 (s, 2H), 8.11 (d, *J* = 7.8 Hz, 2H), 8.02 (t, *J* = 7.8 Hz, 1H), 7.52 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H), 6.98 (s, 4H), 6.10 (d, *J* = 8.3 Hz, 2H), 2.31 (s, 6H), 2.26 (s, 12H). ^{13}C NMR (175 MHz, CD_2Cl_2) δ: 158.9, 153.3, 150.6, 139.0, 138.5, 136.9, 136.7, 134.2, 129.5, 122.1, 110.6, 108.3, 21.1, 18.7. IR (CH_2Cl_2, cm^{-1}): 3234 (N-H). UV-vis (THF): 519 nm (425 M^{-1}cm^{-1}), 378 nm (17900 M^{-1}cm^{-1}), 276 nm (28300 M^{-1}cm^{-1}), 249 nm (29500 M^{-1}cm^{-1}). Anal. calcd for C33H33ClCuN5: C, 66.21; H, 5.56; N, 11.70. Found: C, 66.48; H, 5.45; N, 11.72.

Synthesis of Cu(H_2Tpy^{NMes})Br (2): The preparation and purification is the same as for **1**. From 50.5 mg (0.101 mmol) of H_2Tpy^{NMes} and 13.8 mg (0.096 mmol) of copper(I) bromide, 48.0 mg (78% yield) of **2** can be obtained as a black crystalline powder. Crystals suitable for X-ray were grown from pentane diffusion into a concentrated toluene solution of **2** at

3°C. ^{1}H NMR (700 MHz, CD_2Cl_2) δ: 8.55 (s, 2H), 8.12 (d, *J* = 7.8 Hz, 2H), 8.03 (t, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 2H), 6.97 (s, 4H), 6.10 (d, *J* = 8.3 Hz, 2H), 2.31 (s, 6H), 2.27 (s, 12H). ^{13}C NMR (175 MHz, CD_2Cl_2) δ: 158.8, 153.5, 150.8, 139.1, 138.7, 137.1, 136.9, 134.0, 129.5, 122.2, 110.8, 108.5, 21.1, 18.8. IR (CH_2Cl_2, cm^{-1}): 3242 (N-H). UV-vis (λ_{max}, nm (ε, M^{-1}cm^{-1})): 378 nm (17100 M^{-1}cm^{-1}), 275 nm (26700 M^{-1}cm^{-1}), 248 nm (27900 M^{-1}cm^{-1}). Anal. calcd for C33H33BrCuN5: C, 61.63; H, 5.17; N, 10.89. Found: C, 61.09; H, 5.30; N, 10.63.

Synthesis of Cu(H_2Tpy^{NMes})I (3): 63.2mg (0.127 mmol) of H_2Tpy^{NMes} in 5mL of THF was added to a vial containing 22.9mg (0.121 mmol) copper(I) iodide. The solution was stirred at room temperature for 18 hrs then the solvent was removed *in vacuo*. After washing the resulting solid with MeCN and pentane, the product was washed through a sintered glass frit with THF and the solution was concentrated, layered with pentane, and stored in a -33°C freezer overnight. Following removal of the supernatant, the product was dried under vacuum providing 59.2mg (71% yield) of a black powder. X-ray quality crystals were obtained from slow diffusion of diethyl ether into a concentrated CH_2Cl_2 solution at 3°C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 8.12 (d, *J* = 7.1 Hz, 2H), 8.03 (t, *J* = 7.1 Hz, 1H), 7.82 (s, 2H), 7.54 (dd, 2H), 7.51 (d, 2H), 6.96 (s, 4H), 6.11 (d, 2H), 2.30 (s, 6H), 2.24 (s, 12H). ^{13}C NMR (175 MHz, CD_2Cl_2) δ: 158.3, 154.2, 151.2, 139.2, 139.0, 137.2, 137.1, 133.5, 129.6, 122.5, 111.5, 108.6, 21.1, 19.1. IR (CH_2Cl_2, cm^{-1}): 3256 (N-H). UV-vis (THF): 371 nm (15000 M^{-1}cm^{-1}), 271 nm (26000 M^{-1}cm^{-1}), 249 nm (26300 M^{-1}cm^{-1}). Anal. calcd for C33H33CuIN5: C, 57.43; H, 4.82; N, 10.15. Found: C, 57.81; H, 4.93; N, 10.04.

Synthesis of [Cu(H_2Tpy^{NMes})Cl]PF_6 (4a): 30.2 mg (0.0505 mmol) of **1** was dissolved in 3mL CH_2Cl_2 and was added to a vial containing a 15.9 mg (0.0480 mmol) ferrocenium hexafluorophosphate in 2 mL CH_2Cl_2. The reaction mixture was stirred for 30 min at room temperature until a dark green solution developed. The CH_2Cl_2 was removed *in vacuo* and the resulting dark green precipitate was transferred to a sintered glass frit with benzene and filtered. The precipitate was then washed with benzene (2 x 2 mL) to remove excess **1** and ferrocene and then pentane. The precipitate was washed through the frit with minimal THF. Diethyl ether was added to precipitate the product over 12 hours in a -33°C freezer. 30.6 mg (89% yield) of a dark brown solid was obtained after decanting the supernatant and drying under vacuum. IR (solid, cm^{-1}): 3251. UV-vis (THF): 765 nm (117 M^{-1}cm^{-1}), 407 nm (18500 M^{-1}cm^{-1}), 275 nm (19400 M^{-1}cm^{-1}), 244 nm (30600 M^{-1}cm^{-1}). ESI-MS (m/z) 597.2 [M-PF_6]$^+$ Anal. calcd for C33H33ClCuF6N5P: C, 53.30; H, 4.47; N, 9.42. Found: C, 53.54; H, 4.63; N, 9.31.

Synthesis of [Cu(H_2Tpy^{NMes})Cl]ClO_4 (4b): *Note that perchlorate salts are potentially explosive and care must be taken when handling dry solids. We used small scale preparations (< 10 mg) to minimize risk associated with this synthesis.*

In the air, 8.2 mg (0.048 mmol) of $CuCl_2 \cdot 2H_2O$ was stirred in 2 mL THF until all dissolved. A solution of 25.1 mg (0.050 mmol) of H_2Tpy^{NMes} in 2 mL THF was then added while stirring at room temperature. A dark orange solid precipitated from the reaction mixture immediately. After 5 min, a solution of 10.9mg (0.053 mmol) AgClO4 in 1 mL THF was added dropwise over 30 seconds. The reaction mixture immediately turned dark brown as much of the precipitate went back into solution. After stirring 30 min at room temperature, the solvent was removed from the reaction mixture via rotary evaporation. The crude product was then brought into the glovebox for recrystallization. 10 mL CH_2Cl_2 was used to dissolve the product and the yellow solution was filtered using a pipette containing glass filter paper. The CH_2Cl_2 was removed *in vacuo* and 1 mL THF was added followed by 6mL ether to precipitate a yellow powder. The supernatant was decanted and the product dried under vacuum to give 25.2 mg (67%) yield. Crystals suitable for X-ray diffraction were grown from slow diffusion of methyl tert-butyl ether into a saturated THF solution. IR (solid, cm^{-1}): 3246. UV-vis (THF): 769 nm (153 $M^{-1}cm^{-1}$), 406 nm (19300 $M^{-1}cm^{-1}$), 276 nm (21800 $M^{-1}cm^{-1}$), 244 nm (34200 $M^{-1}cm^{-1}$). ESI-MS (m/z) 597.2 $[M-ClO_4]^+$ Anal. calcd for C33H33Cl2CuN5O4: C, 56.78; H, 4.76; N, 10.03. Found: C, 56.72; H, 4.70; N, 10.00.

Synthesis of 6,6"-bis(2,4,6-trimethylphenoxy)terpyridine (Tpy^{OMes}): Potassium 2,4,6-trimethylphenoxide was prepared prior to the experiment by allowing 937.1 mg (6.88 mmol) 2,4,6-trimethylphenol to react with 746.6 mg (5.73 mmol) of benzyl potassium in THF. The reaction was stirred for 5 min, followed by removal of the solvent *in vacuo* to afford a colorless oil. Benzene (*ca.* 10 mL) was added to precipitate the product as a white solid. The product was washed with benzene (3 x 5 mL) and pentane (3 x 5 mL), dried under vacuum, and used without further purification for the next step. A 20 mL scintillation vial was charged with 150.7 mg (0.385 mmol) 6,6"-dibromoterpyridine, 167 mg (0.963 mmol) potassium 2,4,6-trimethylphenoxide, 36.6 mg (0.193 mmol) copper(I) iodide, and 10 mL toluene. The vial was capped and the mixture was heated at 80°C for 18 hours. The reaction mixture was then removed from the glovebox and, in the air, the reaction mixture was passed through a plug of neutral alumina (4 x 3 cm) and the alumina was washed with CH_2Cl_2 (20 mL). Solvent was removed from the colorless organic filtrate by rotatory evaporation. The oil was triturated with pentane to afford 165 mg (85% yield) of a white crystalline powder after drying under vacuum. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.27 (d, *J* = 7.4 Hz, 2H), 8.11 (d, *J* = 7.8 Hz, 2H), 7.77 (dd, *J* = 8.1, 7.4 Hz, 2H), 7.75 (t, *J* = 7.8 Hz, 1H), 6.93 (s, 4H), 6.70 (d, *J* = 8.1 Hz, 2H), 2.33 (s, 6H), 2.13 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.9, 154.9, 154.8, 148.4, 140.3, 137.9, 134.6, 130.9, 129.4, 121.3, 114.9, 109.0, 21.0, 16.7. Anal. calcd for C33H31N3O2: C, 79.02; H, 6.23; N, 8.38. Found: C, 79.20; H, 6.33; N, 8.30.

Synthesis of $[Cu(Tpy^{OMes})Cl]ClO_4$ (5): *Note that perchlorate salts are potentially explosive and care must be taken when handling dry solids. We used small scale preparations (< 10 mg) to minimize risk associated with this synthesis.*
In the air, 5.9 mg (0.0347 mmol) $CuCl_2 \cdot 2H_2O$ was stirred in 2 mL THF until complete dissolution. To this mixture was added a solution of 17.4 mg (0.0347 mmol) Tpy^{OMes} in 2 mL THF while stirring at room temperature. A yellow solid precipitated from the reaction mixture immediately. After 5 min, a solution of 7.2 mg (0.0347 mmol) $AgClO_4$ in 1 mL THF was added dropwise over 30 seconds. After stirring for 2 minutes, the reaction mixture was filtered through 545 celite and the solvent was removed via rotary evaporation. A minimal amount of THF (*ca*. 1 mL) was added to the dry reaction mixture and the solution was filtered through 545 celite, and diethyl ether was allowed to diffuse into this solution at 3°C, green crystals suitable for X-ray were obtained. Note: as noted in the main text, solutions of this compound (from X-ray quality crystals) are not stable, and exist as a mixture of disproportionation products ($CuCl_2$ and **6**). Furthermore, solutions (THF or DCM) of this complex slowly precipitate a light green solid that we have identified as a to **6**

and free $CuCl_2$ by cyclic voltammetry, ESI-MS, and EPR spectroscopy. ESI-MS (m/z) 599.1 $[M-ClO_4]^+$

Synthesis of $[Cu(Tpy^{OMes})_2](ClO_4)_2$ (6): *Note that perchlorate salts are potentially explosive and care must be taken when handling dry solids. We used small scale preparations (< 10 mg) to minimize risk associated with this synthesis.*

In the air, 3.1 mg (0.0183 mmol) $CuCl_2 \cdot 2H_2O$ was dissolved in 2 mL THF in a 20 mL scintillation vial at room temperature. 7.6 mg (0.0366 mmol) of AgClO4 was then dissolved in 1 mL THF and added to the stirring $CuCl_2$ solution. After 5 min, the solution was filtered with a glass pipette fitted with glass filter paper into a new 20 mL scintillation vial. A solution of 18.4 mg (0.0366 mmol) Tpy^{OMes} in 1 mL THF was then added dropwise over 30 seconds, immediately precipitating a light green solid. The reaction mixture was stirred for 30 min at room temperature. The light green precipitate was collected on a sintered glass frit and washed with THF (3 x 3 mL) and pentane (3 x 3 mL) then passed through the frit with CH_2Cl_2. The solvent was removed *in vacuo* providing 22.6mg (97% yield) of a light green powder. UV-vis (CH_2Cl_2): 734 nm (50 $M^{-1}cm^{-1}$), 355 nm (70700 $M^{-1}cm^{-1}$), 341 nm (62700 $M^{-1}cm^{-1}$), ESI-MS (m/z) 532.7 $[M-2ClO_4]^{2+}$ Anal. calcd for C66H66Cl2CuN6O12: C, 62.63; H, 4.94; N, 6.64. Found: C, 62.73; H, 4.89; N, 6.50.

Synthesis of $[Cu_6(dhtp)_4](CuCl_2)_2$ ($Cu_6(dhtp)_4$): 4.6 mg (0.046 mmol) CuCl and 12.2mg (0.046 mmol) was stirred in 4 mL methanol for 1 hour at room temperature. The solvent was then removed *in vacuo*. A red solid was collected. Red crystals suitable for X-ray diffraction were grown from slow diffusion of diethyl ether into a concentrated DMF solution. ^1H NMR (400 MHz, DMSO-d_6) δ: 12.50 (s, 4H), 8.16 (d, 4H), 8.10 (t, 2H), 7.59 (dd, 4H), 7.07 (d, 4H), 6.49 (d, 4H).

NMR Data:

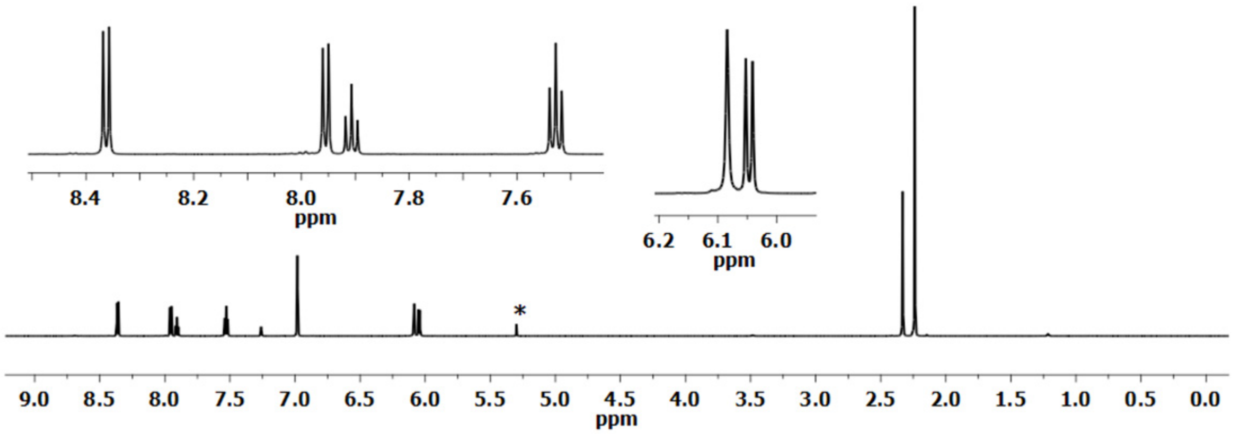


Figure S1: 700 MHz ^{1}H NMR spectrum of H_2Tpy^{NMes} collected at 25°C in $CDCl_3$. (*trace CH_2Cl_2)

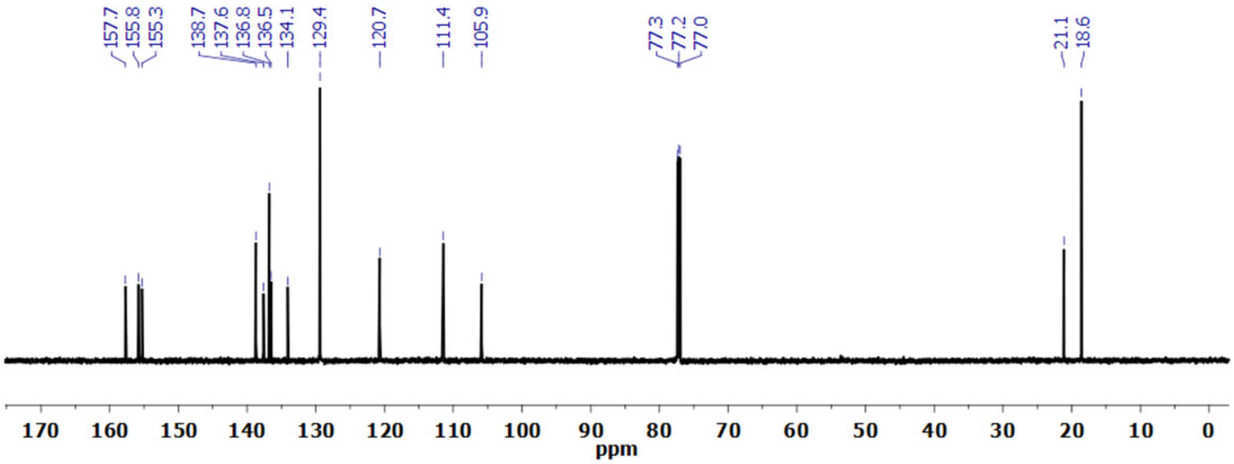


Figure S2: 175 MHz ^{13}C NMR spectrum of H_2Tpy^{NMes} collected at 25°C in $CDCl_3$.

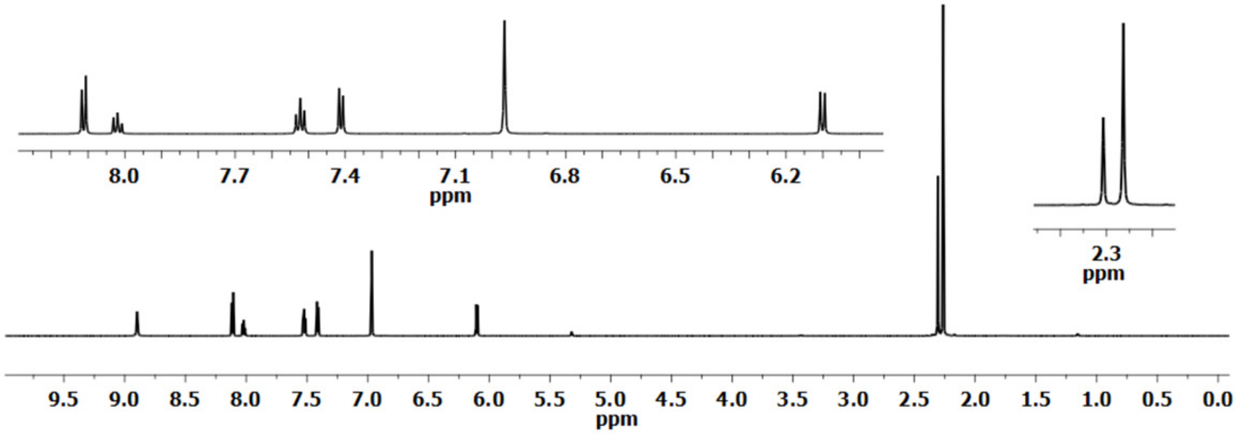


Figure S3: 700 MHz ^{1}H NMR spectrum of Cu(H_2Tpy^{NMes})Cl (**1**) collected at 25°C in CD_2Cl_2.

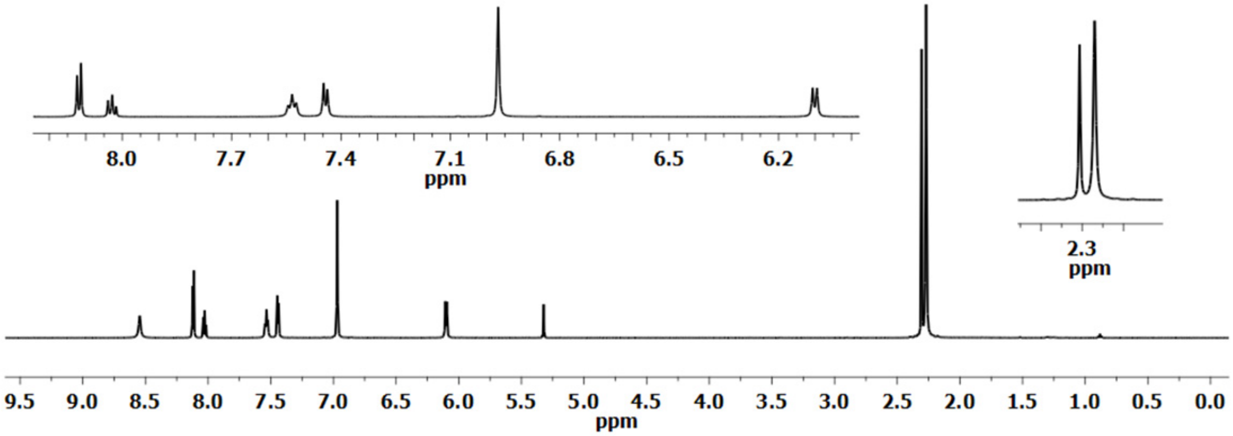


Figure S4: 700 MHz ^{1}H NMR spectrum of Cu(H_2Tpy^{NMes})Br (**2**) collected at 25°C in CD_2Cl_2.

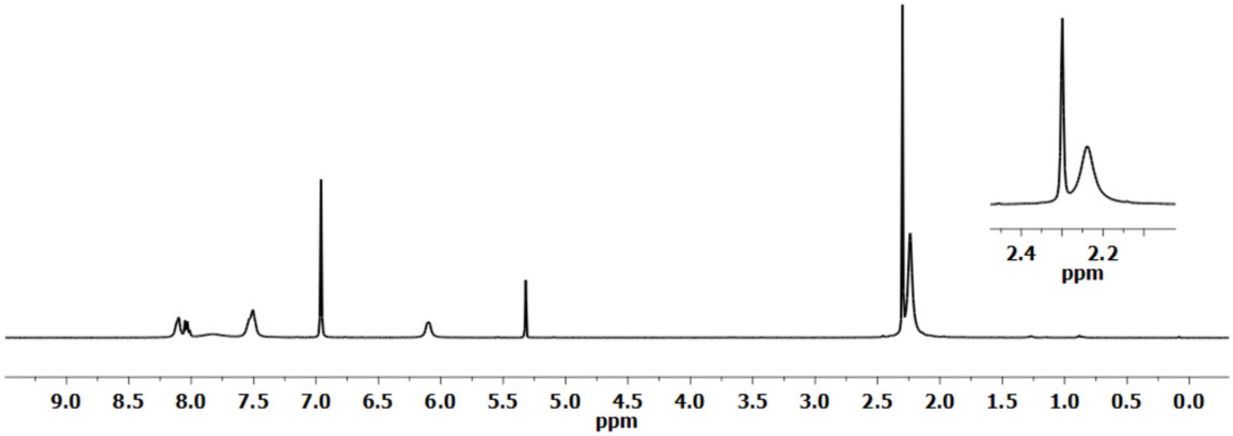


Figure S5: 400 MHz ^{1}H NMR spectrum of Cu(H_2Tpy^{NMes})I (**3**) collected at 25°C in CD_2Cl_2.

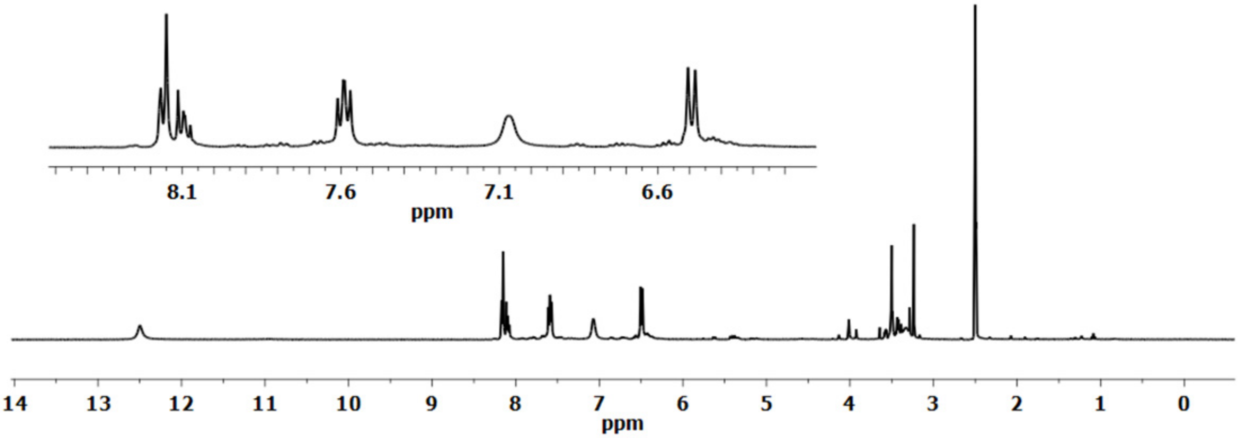


Figure S6: 400 MHz ^1H NMR spectrum of $Cu_6(dhtp)_4$ collected at 25°C in DMSO-d_6.

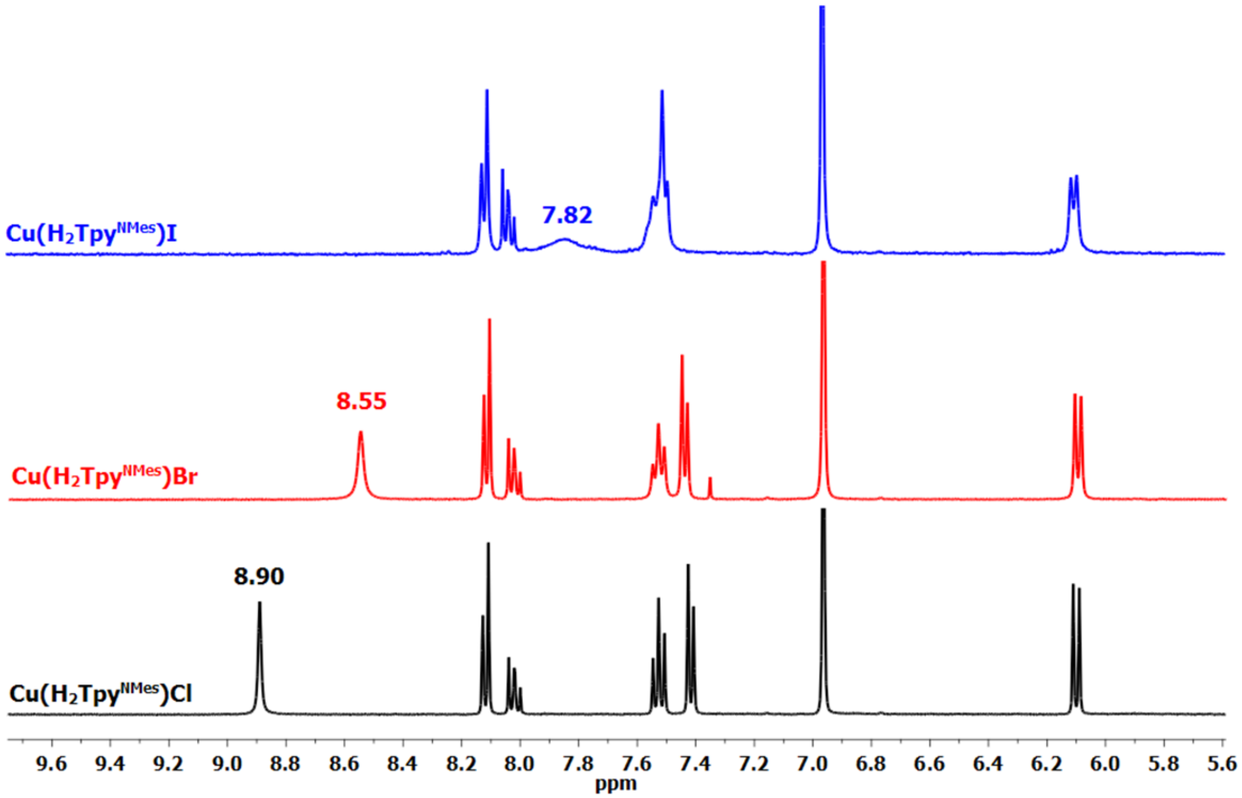


Figure S7: ^1H NMR (400 MHz) spectra overlay of the aromatic region of **1** (black), **2** (red), and **3** (blue) collected at 25°C in CD_2Cl_2 showing the shift in the N-H proton resonance with varying halide ligands.

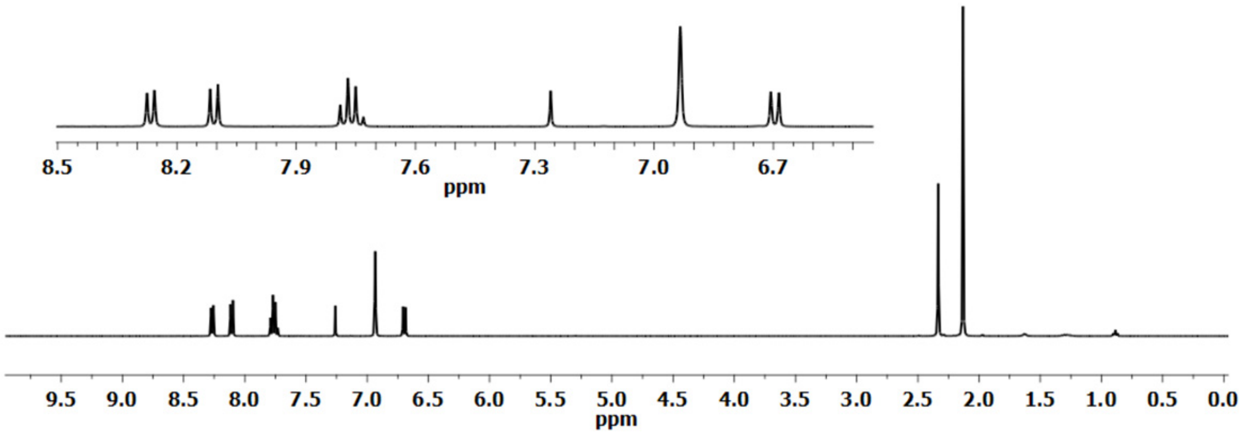


Figure S8: 400 MHz ^{1}H NMR spectrum of Tpy^{OMes} collected at 25°C in CDCl$_3$.

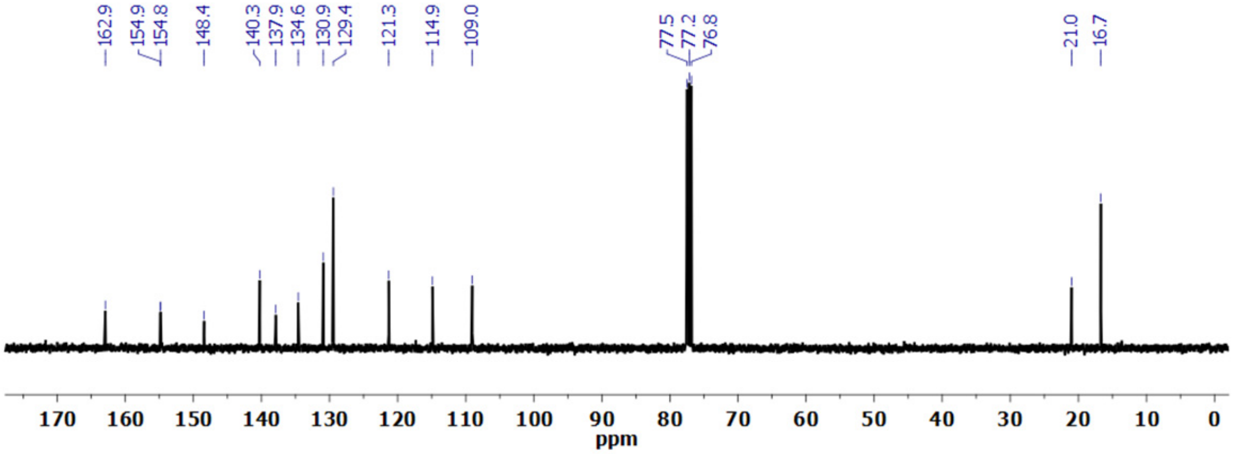


Figure S9: 100 MHz ^{13}C NMR spectrum of Tpy^{OMes} collected at 25°C in CDCl$_3$.

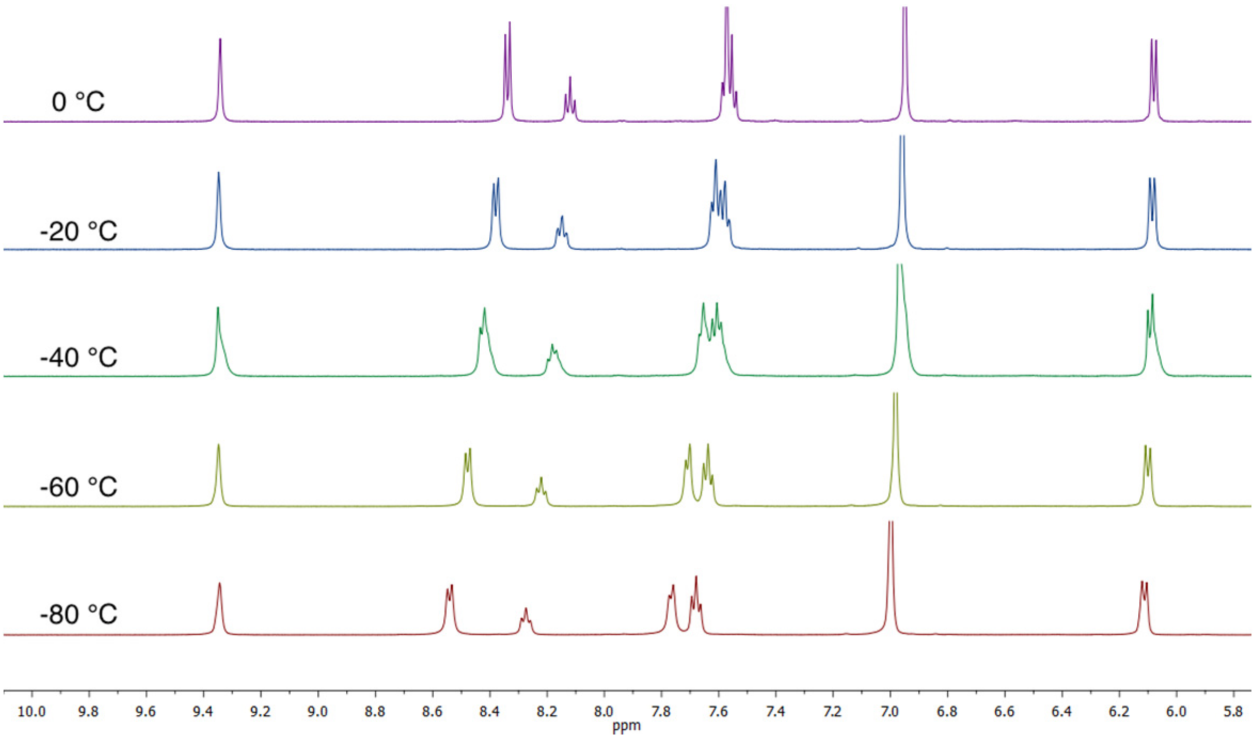


Figure S10: Variable temperature ^{1}H NMR (500 MHz) spectra of **1** in THF-d_8.

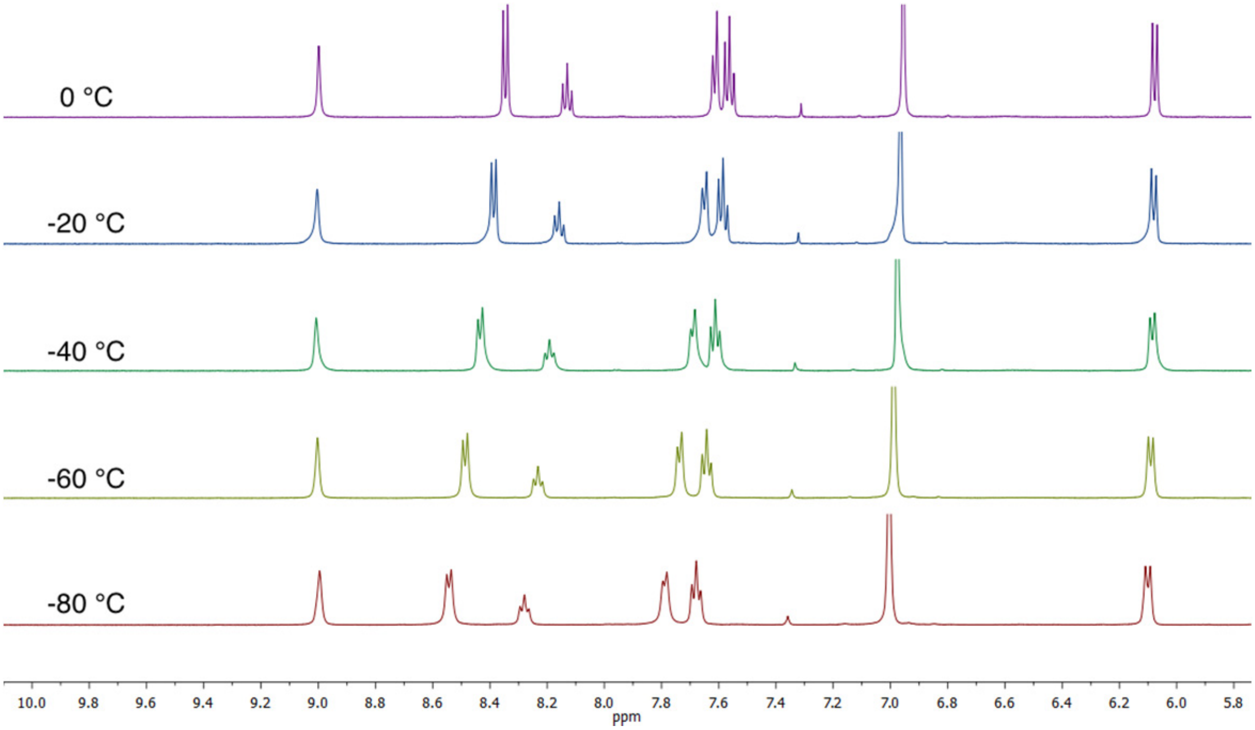


Figure S11: Variable temperature ^{1}H NMR (500 MHz) spectra of **2** in THF-d_8.

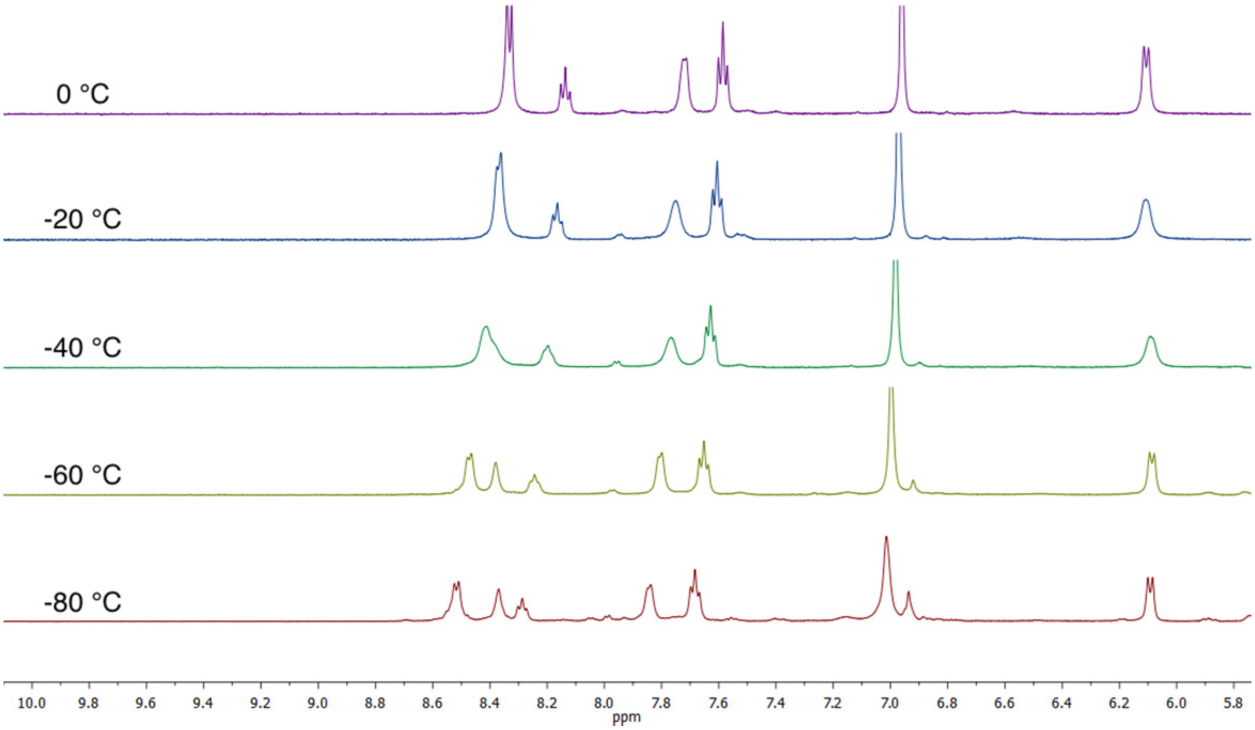


Figure S12: Variable temperature ^{1}H NMR (500 MHz) spectra of **3** in THF-d_8.

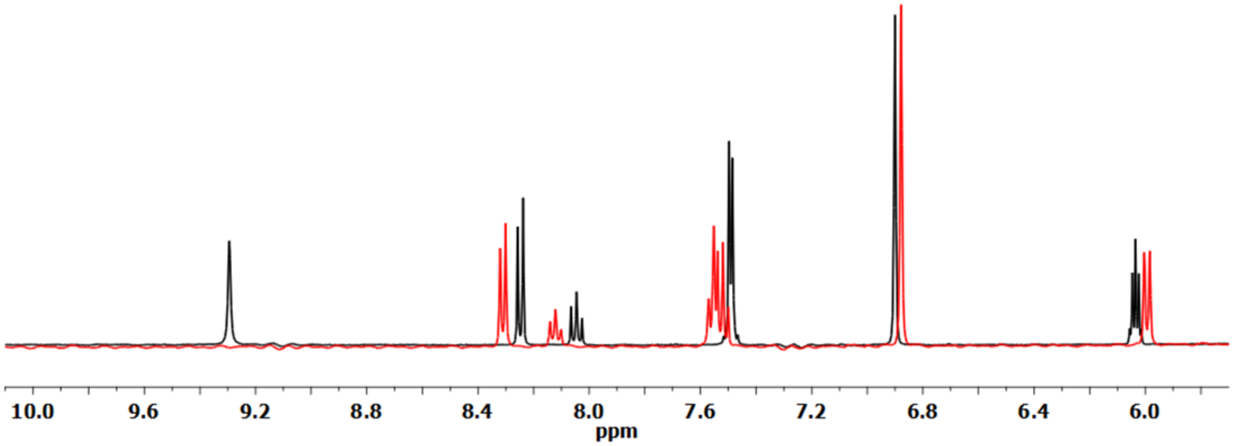
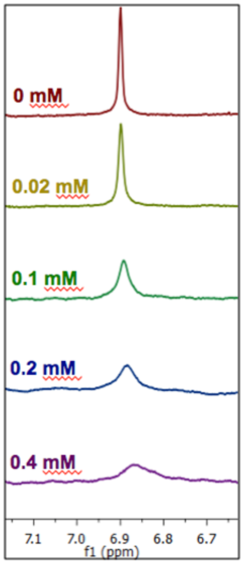
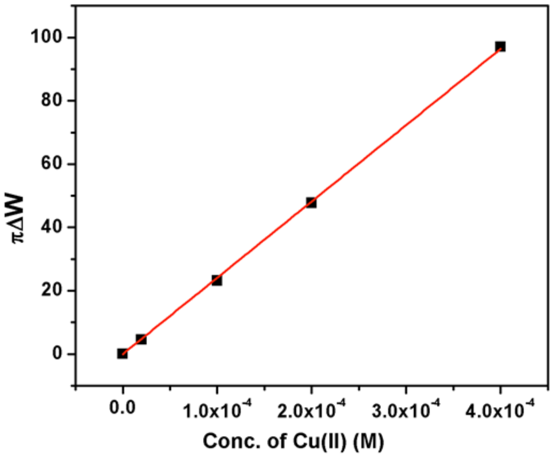


Figure S13: ^{1}H NMR (400 MHz) spectra of the aromatic region of **1** in THF before (black) and after (red) adding a drop of D_2O. The downfield peak at 9.3 ppm disappears after addition of D_2O, consistent with an NH group in rapid exchange with deuterium in solution.

Electron Transfer Self-Exchange Kinetics for 1:

Electron transfer self-exchange was measured by an NMR line broadening experiment. 600 μL of a 2.33 mM solution of **1** in THF was added to five NMR tubes. The tubes were then diluted with 100 μL of THF and **4a** so that the concentration of **4a** in the tubes was as follows: 0.00 mM, 0.02 mM, 0.1 mM, 0.2 mM, 0.4 mM. The concentration of **1** was maintained at 2.0 mM following dilution. The ^{1}H NMR spectrum was obtained for each sample and the broadening of the aromatic mesityl peak at 6.9 ppm was monitored. Each peak was fit with the line fitting function in MestReNova to obtain a peak width at half height in Hz. The peak widths were then plotted using the equation $\pi\Delta W_{dp} = \pi W_d + k_{11}[Cu^{II}]$ where Wd is the peak width for the diamagnetic sample (0.00 mM **4a**) and ΔW_{dp} is change in peak width between the diamagnetic sample and the samples containing Cu^{II} (p=paramagnetic). The slope of the resulting plot provided an ET self-exchange rate of $k_{11} = 2.4 \times 10^5\ M^{-1}s^{-1}$.





Infrared Spectroscopy:

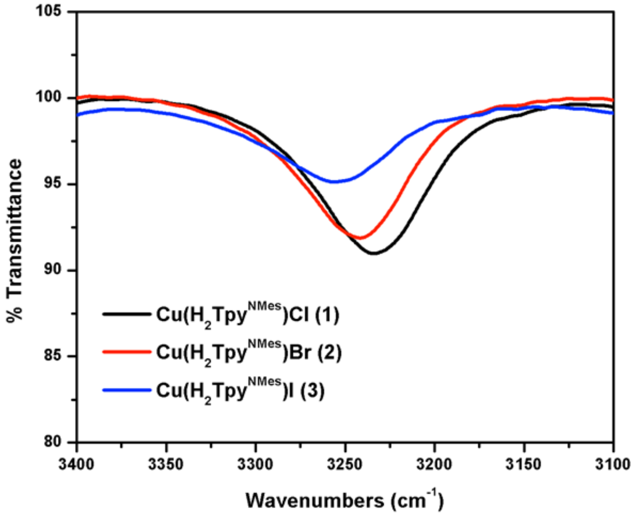


Figure S14: Infrared spectrum overlay of **1**, **2** and **3** collected in CH_2Cl_2. The N-H region is shown to show shift of N-H stretching frequency.

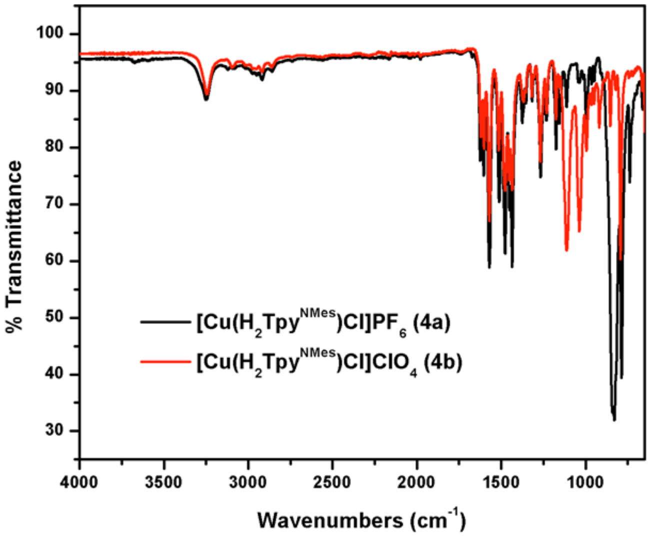


Figure S15: Infrared spectra overlay of **4a** and **4b** collected on solid samples.

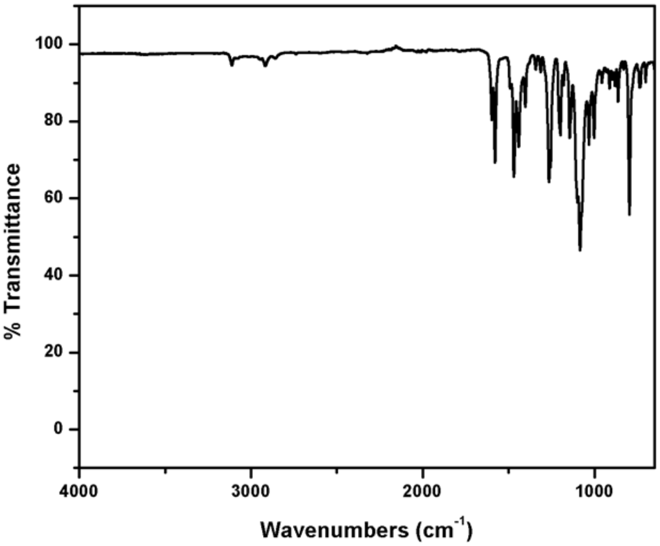


Figure S16: Infrared spectrum of **6** collected with a solid sample.

UV-Vis Spectroscopy:

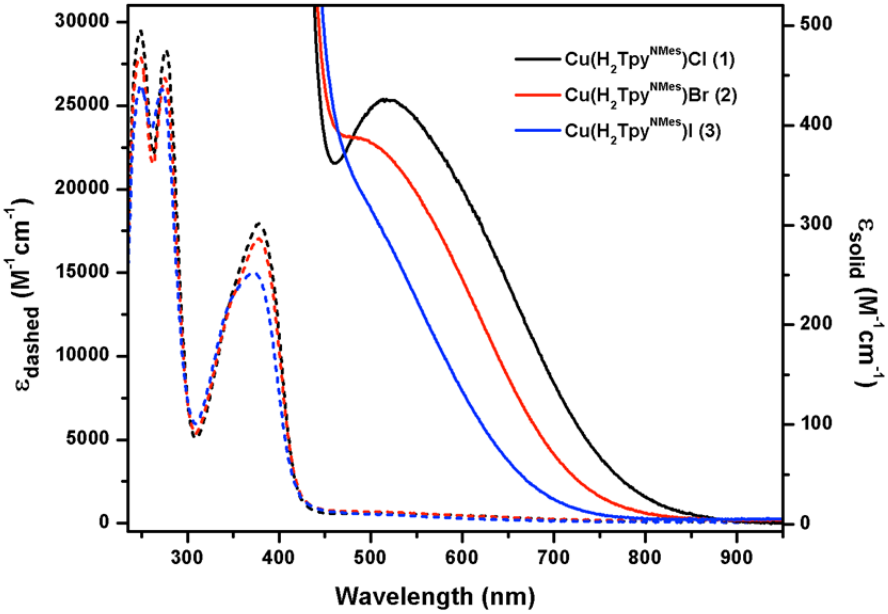


Figure S17: UV-Vis spectra overlay collected in THF of **1**, **2**, and **3**. The solid traces correspond to 3.0 mM solutions and the dashed traces to 0.05 mM solution.

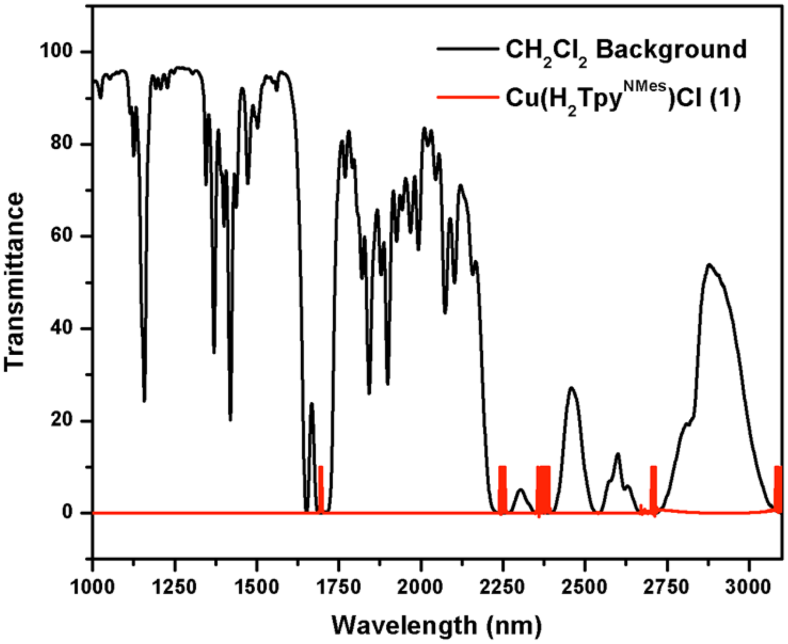


Figure S18: Near-infrared spectrum of **1** in CH_2Cl_2 (2 mM) overlaid with the baseline spectrum to show regions that do not contain relevant data.

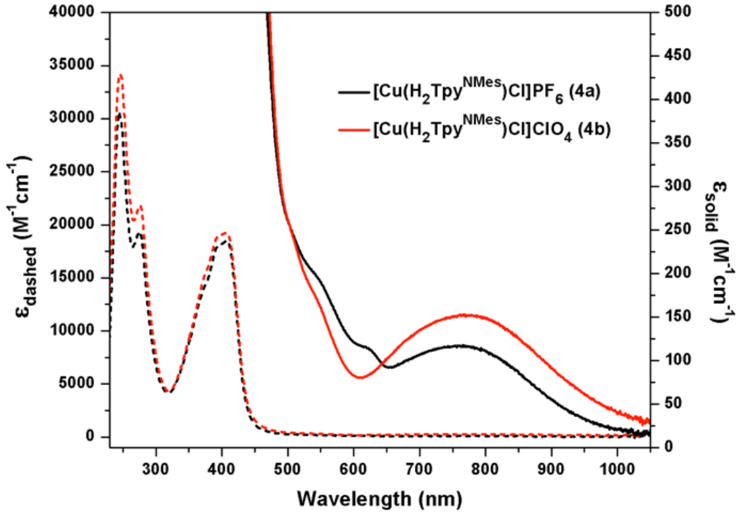


Figure S19: UV-Vis spectra overlay collected in THF of **4a** and **4b**. The solid traces correspond to 2.0 mM solutions and the dashed traces to 0.05 mM solution.

Electrochemistry:

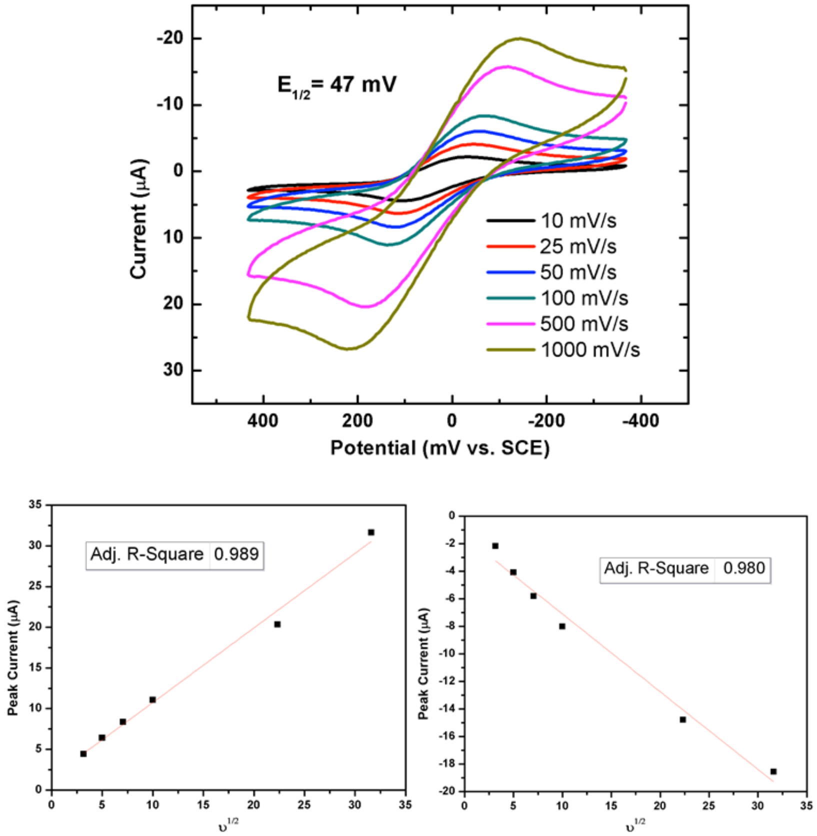


Figure S20: (Top) Cyclic voltammograms of **1** in 0.1M TBAPF$_6$ CH$_2$Cl$_2$ at varying scan rates. (Bottom) Peak heights plotted versus square root of scan rate for anodic (left) and cathodic (right) sweeps.

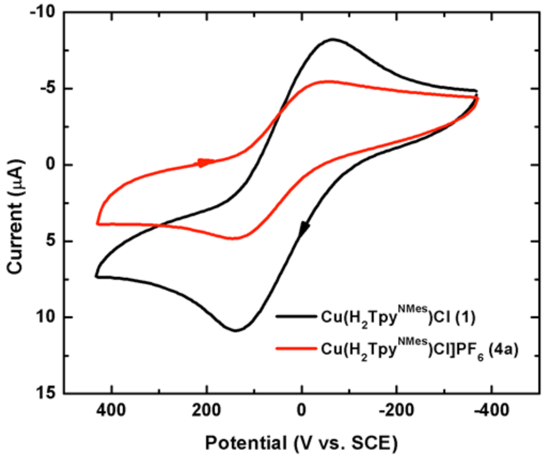


Figure S21: Cyclic voltammograms of **1** and **4a** in 0.1M TBAPF$_6$ CH$_2$Cl$_2$ showing reversible Cu$^{I/II}$ couple from starting from either material.

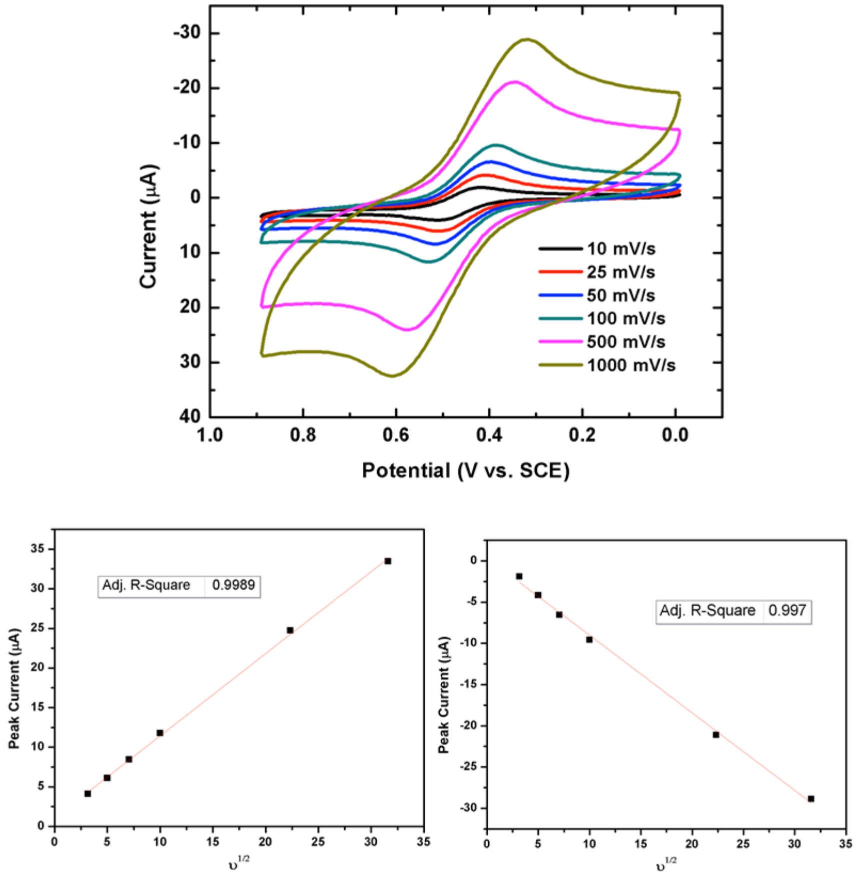


Figure S22: (Top) Cyclic voltammograms of ferrocene in 0.1M TBAPF$_6$ CH$_2$Cl$_2$ at varying scan rates. (Bottom) Peak heights plotted versus square root of scan rate for anodic (left) and cathodic (right) sweeps.

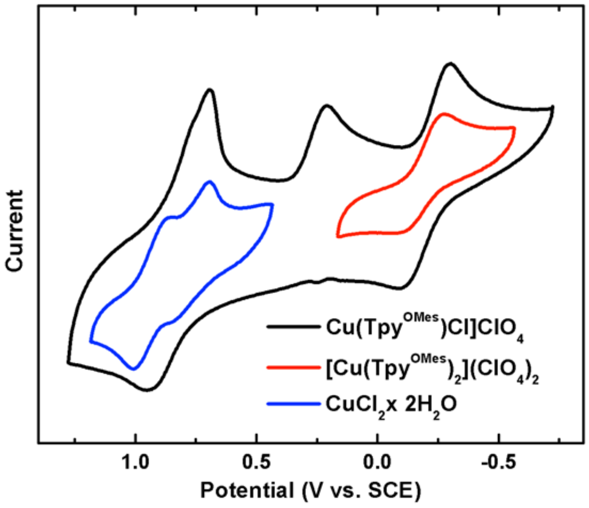


Figure S23: Cyclic voltammograms of **5**, **6**, and free $CuCl_2$ in 0.1M $TBAClO_4$ CH_2Cl_2 showing the presence of both **6** and $CuCl_2$ in samples of **5**.

EPR:

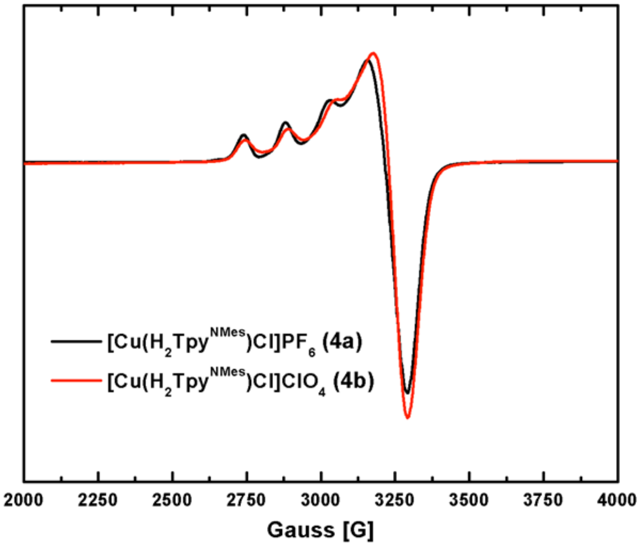


Figure S24: EPR overlay of **4a** and **4b** collected in THF at 120K.

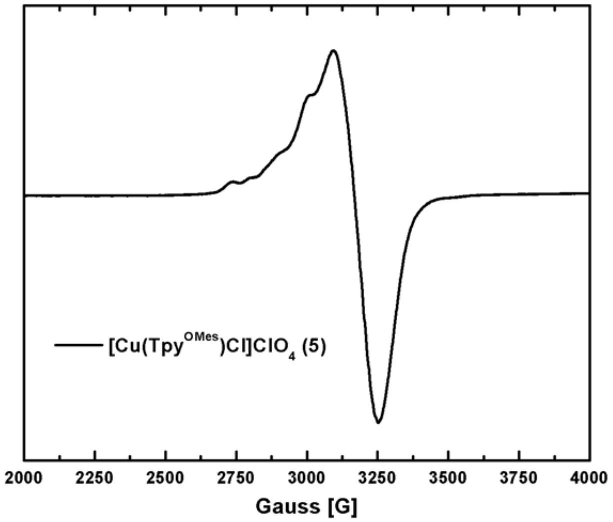


Figure S25: EPR spectrum of **5** collected in CH_2Cl_2 at 120K. Sample was prepared by dissolving **5** in CH_2Cl_2, quickly filtering, and freezing in liquid N_2.

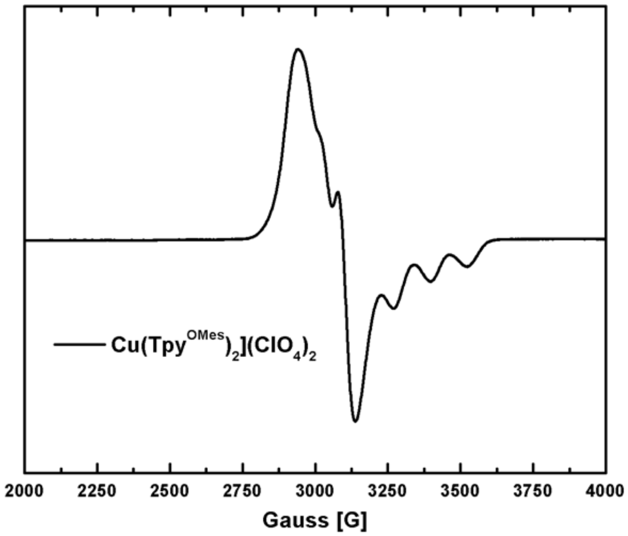


Figure S26: EPR spectrum of **6** collected in CH_2Cl_2 at 120K.

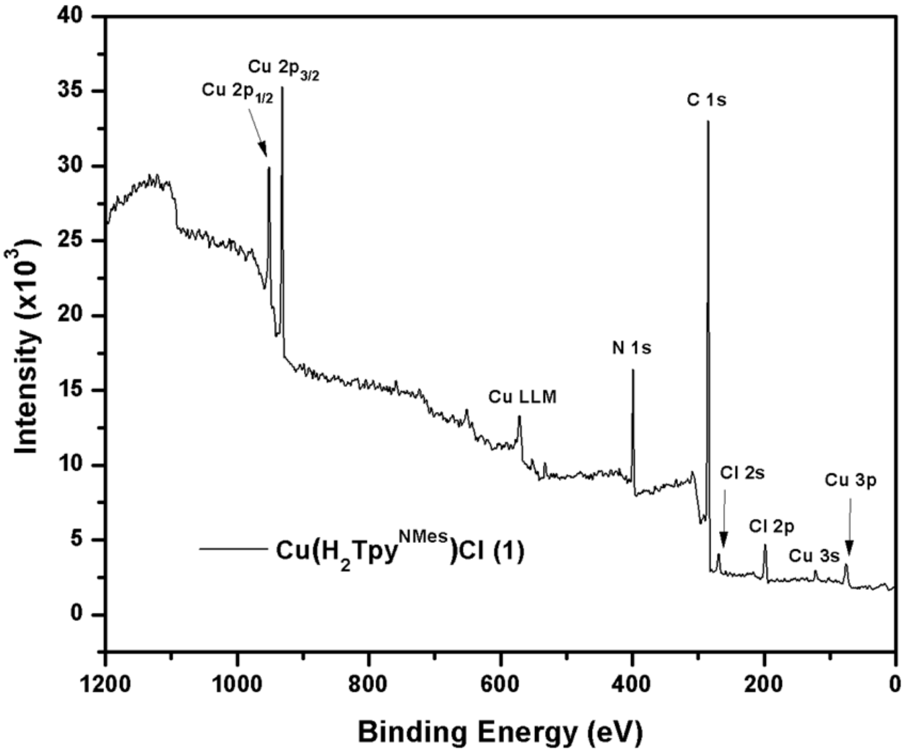


Figure S27: XPS spectrum of **1**.

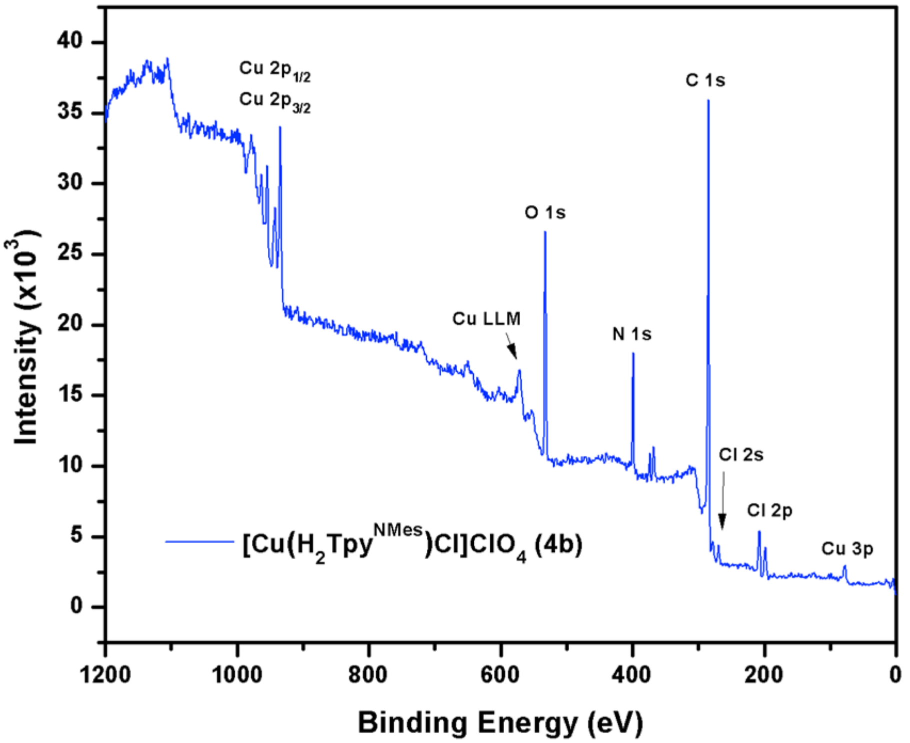


Figure S28: XPS spectrum of **4b**.

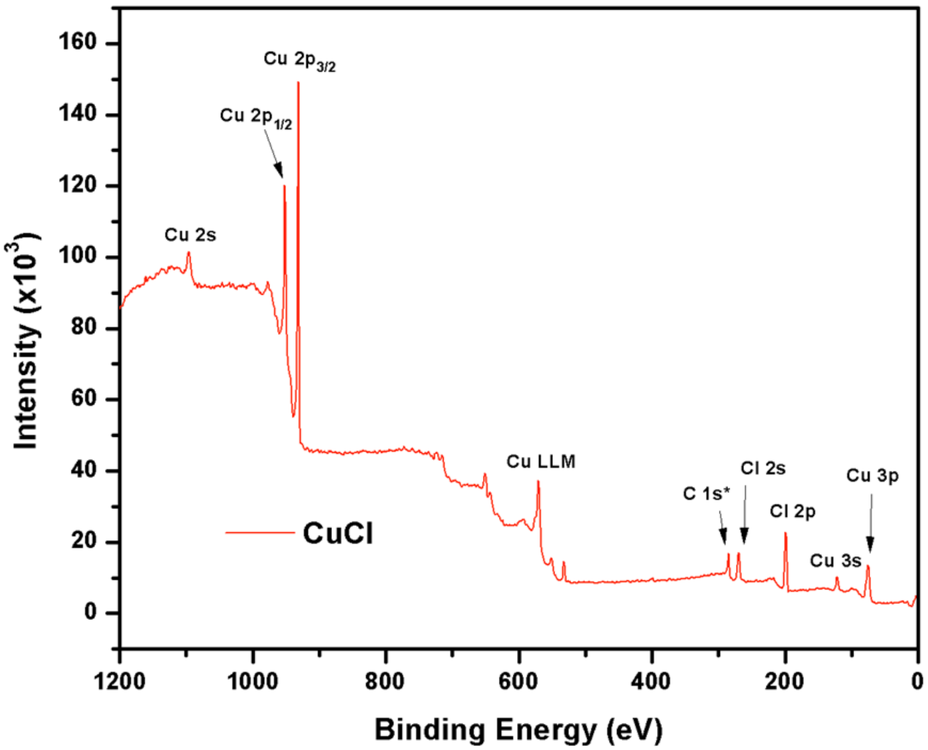


Figure S29: XPS spectrum of CuCl salt. (*adventitious carbon for reference)

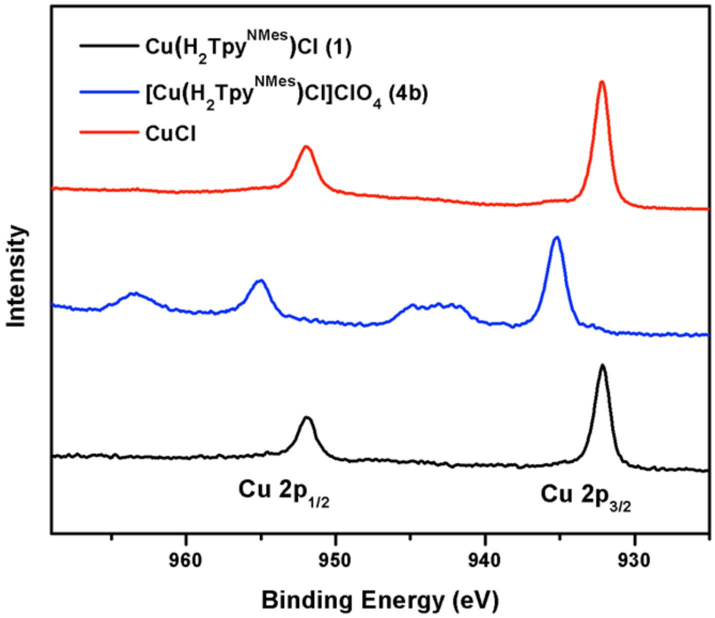


Figure S30: Overlay of the Cu 2p region of the XPS spectrum for **1**, **4b**, and CuCl.

Computational Details:

All calculations were performed using Gaussian 09[4] and visualized in GaussView. The atoms C and H were calculated to the double-zeta level of theory with the Pople basis set 6-31G(d,p)[5] and the primary sphere atoms Cu, N, and Cl were calculated to the triple-zeta level of theory with the Ahlrich basis set def2-TZVP.[6] Structure benchmarking was performed with Lee, Yang, and Parr's functional (B3LYP)[7], Truhlar and Zhao's pure (M06L)[8] and hybrid (M06)[9] functional, and Head-Gordon's long range-corrected functional (wB97XD).[10] Spin-unrestricted structures were freely optimized in C_1 symmetry from coordinates generated from the X-ray structure using a polarizable continuum model (PCM) of CH_2Cl_2. Optimized structures were verified to be minima on the potential energy surface (PES) by absence of imaginary frequencies in the calculated vibrational spectra and/or by independent stability calculations.

Structural Benchmarking:

Benchmarking was performed to determine the functional that best predicts the observed geometry of **1**. Hybrid functionals with varying Hartree-Fock contributions (20-27%) were used along with the M06L pure functional. The 6-31G and def2-TZVP basis sets were chosen because of their successful use in a similar system.[11] Results for the optimized geometric parameters are given in Table 1. The M06 and wB97XD functionals gave the best parameters with τ_4 values, angles, and bond lengths closely resembling the crystal structure of **1**. The M06, wB97XD, and B3LYP functionals were used for the singlet ground state analysis.

Table S1: Calculated geometric parameters for varying functionals compared to the crystal structure parameters of **1**.

Parameter	**XRD**	**B3LYP**	**M06**	**M06L**	**wB97XD**
N2-Cu-Cl Angle	169.78	173.887	169.703	160.643	169.636
N1-Cu-N3 Angle	147.52	149.083	146.436	145.59	146.445
τ_4 value	**0.303**	**0.263**	**0.311**	**0.381**	**0.311**
N1-Cu bond length (Å)	2.318	2.37743	2.35182	2.25766	2.34149
N2-Cu bond length (Å)	2.023	2.06157	2.05015	2.04199	2.07587
N3-Cu bond length (Å)	2.315	2.38705	2.33152	2.24468	2.33871
Cl-Cu bond length (Å)	2.214	2.27033	2.22932	2.2553	2.25739
N4-Cl bond length (Å)	3.26	3.3308	3.32379	3.29754	3.30917
N5-Cl bond length (Å)	3.353	3.33232	3.32161	3.3161	3.30883

Computational Analysis of the Singlet Ground State:

The following studies were performed to supplement the bond length analysis, UV-Vis/near-IR data, and XPS data in assigning the formal oxidation state of the Cu center in **1.** Complex **1** could be described as either the proposed closed-shell singlet Cu(I), or as a triplet or open-shell singlet (broken symmetry state) Cu(II)-ligand radical species. All spin-unrestricted geometry optimizations produced the closed-shell Cu(I) singlet as the minimum energy state. Using the three hybrid functionals from the benchmark analysis, spin-unrestricted stability calculations were performed on the respective optimized geometries. These calculations scan the PES for alternative spin conformations that are lower in energy. *All three stability calculations maintained that the closed-shell singlet state is the lowest energy state, supporting the oxidation state assignment as Cu(I) from the other characterization methods.*

In addition to stability calculations, geometry optimizations on the triplet diradical state were performed using the same three hybrid functionals in order to compare the relative energy of the states (singlet-triplet gap) and the corresponding geometry. The calculated singlet energies were compared to the triplet energies and the difference was tabulated in Table S2. *The triplet state is on average ~32 kcal/mol higher in energy than the closed-shell singlet.* Note that the optimized geometry of the triplet diradical state deviates significantly from the crystal structure of **1** and the optimized singlet geometry (Figure S31). This geometrical mismatch between the triplet diradical state and the observed solid state geometry likely also persists in the open shell singlet state (the geometric coordinates for the broken symmetry solutions are provided by the triplet structures), which further supports the assignment of the Cu center in **1** to be +1.

Table S2: Comparison of the singlet-triplet gap energy for the various functionals.

Functional	B3LYP	wB97xd	M06
Energy Difference (kcal/mol)	29.65	31.95	34.22

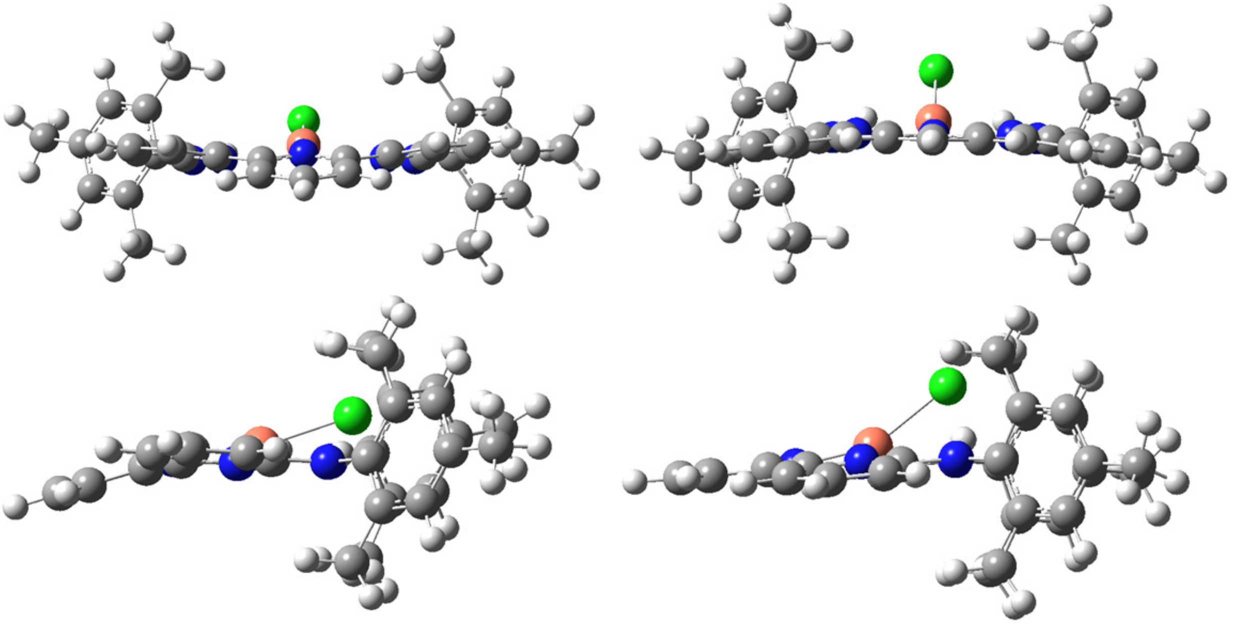


Figure S31: Representative optimized structures (wB97XD functional) for the singlet (left) and triplet (right) state showing ligand distortions in the singlet state.

Crystallographic Details:

Crystals were mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer with a low temperature apparatus and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). Samples were measured at 85(2)K. The data were processed with CrystalClear 2.0[12] and corrected for absorption. Structures were solved in Olex2[13] using the XL refinement program[14]. The SQUEEZE[15] function found in PLATON was used to model residual electron density caused by disordered solvent in **5** and $Cu_6(dhtp)_4$.

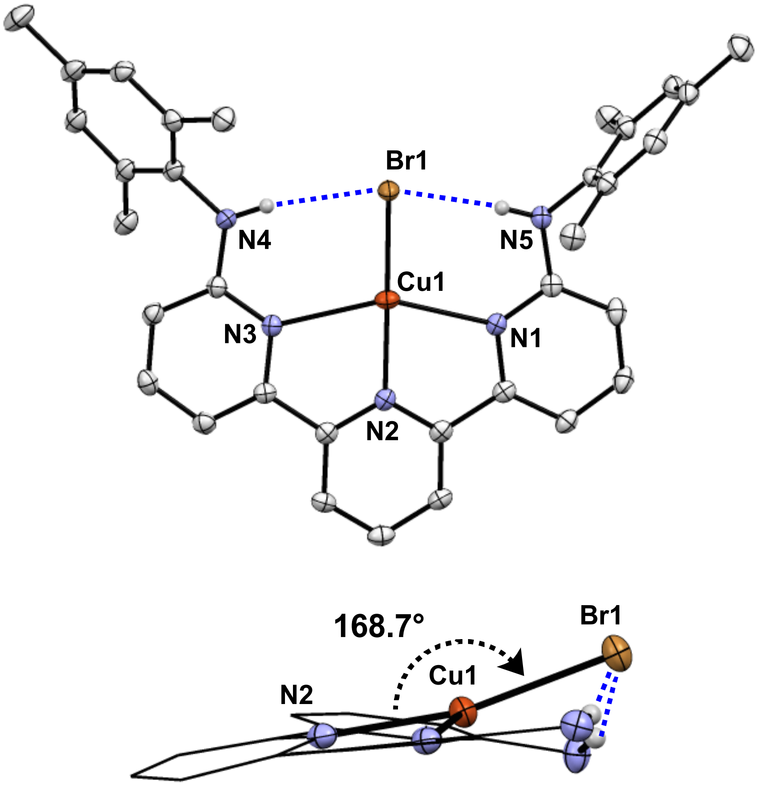


Figure S32: Crystal structure and side-on view of **2**. (50% ellipsoids, H atoms not involved in H-bonding have been omitted for clarity).

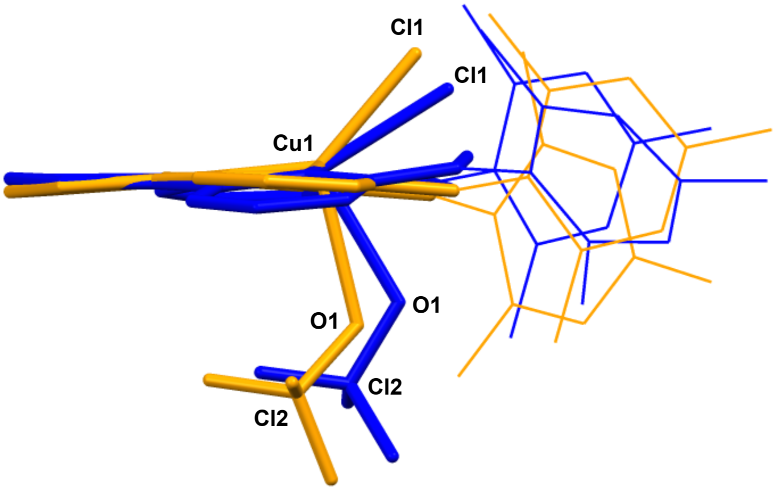


Figure S33: Crystal structure overlay of **4b** and **5** as side-on view. (H atoms not involved in H-bonding have been omitted for clarity).

Table S3: Atomic coordinates for DFT-calculated structures

uwB97XD singlet state				**uwB97XD triplet state**			
Atom	x	y	z	Atom	x	y	z
Cu	6.093574	-1.241977	6.100032	Cu	5.827064	-1.081786	6.519511
Cl	5.743645	-2.653792	4.373718	Cl	4.704592	-2.547771	5.182015
N	5.539573	0.890754	5.308104	N	5.372674	0.744066	5.569066
N	6.065992	-0.035341	7.788977	N	6.004333	0.106404	7.977586
N	7.199664	-2.483799	7.744385	N	6.825859	-2.318995	7.809105
N	7.783222	-4.269554	6.418405	N	7.303402	-4.026948	6.311278
H	7.304112	-3.765397	5.678865	H	6.544003	-3.6646	5.74889
N	5.515886	0.377544	3.067079	N	5.358282	-0.017425	3.37918
H	5.737936	-0.567913	3.362113	H	5.292397	-0.95153	3.76617
C	5.172213	1.235021	4.067318	C	5.196768	1.003325	4.258098
C	4.473829	2.436143	3.812041	C	4.877182	2.303693	3.810177
H	4.192292	2.692881	2.798029	H	4.726805	2.47773	2.752439
C	4.145067	3.242014	4.879398	C	4.751356	3.315172	4.733755
H	3.590285	4.159763	4.713485	H	4.501298	4.318827	4.406176
C	4.516455	2.87463	6.175546	C	4.954503	3.051829	6.089508
H	4.238876	3.489754	7.021584	H	4.887121	3.842995	6.824119
C	5.227196	1.693538	6.333901	C	5.269815	1.760136	6.466727
C	5.726786	1.252139	7.668635	C	5.588741	1.385989	7.8606
C	5.88463	2.146077	8.726936	C	5.533042	2.213885	8.952876
H	5.640458	3.194082	8.609897	H	5.195765	3.239077	8.8686
C	6.407395	1.678545	9.923772	C	5.938093	1.692606	10.214413
H	6.555098	2.356054	10.757556	H	5.893725	2.325214	11.093943

C	6.775249	0.345332	10.030032	C	6.395987	0.401989	10.316354
H	7.228955	-0.025141	10.940287	H	6.717793	0.011465	11.275347
C	6.592139	-0.492041	8.93012	C	6.445243	-0.418156	9.166449
C	7.02008	-1.921403	8.946837	C	6.934908	-1.750126	9.066345
C	7.239999	-2.601961	10.135735	C	7.543767	-2.448703	10.126417
H	7.051915	-2.142985	11.097409	H	7.624804	-1.988857	11.103597
C	7.698874	-3.919522	10.056678	C	8.059098	-3.702955	9.889511
H	7.88593	-4.48344	10.964771	H	8.532796	-4.25741	10.693634
C	7.904104	-4.507001	8.828152	C	7.98292	-4.267097	8.61325
H	8.254516	-5.527987	8.738488	H	8.378012	-5.252701	8.405279
C	7.622935	-3.75193	7.667578	C	7.366017	-3.540468	7.59021
C	8.126429	-5.631112	6.180376	C	7.830725	-5.294025	5.939839
C	7.109991	-6.57723	5.979923	C	6.966145	-6.388734	5.791794
C	7.472731	-7.898366	5.727085	C	7.50181	-7.612567	5.393077
H	6.692395	-8.63877	5.565065	H	6.835608	-8.463875	5.271531
C	8.81119	-8.296503	5.686819	C	8.868364	-7.774797	5.16123
C	9.796951	-7.335536	5.904574	C	9.703455	-6.6698	5.324742
H	10.843858	-7.628744	5.875125	H	10.770063	-6.777358	5.140716
C	9.476928	-5.99844	6.149079	C	9.207294	-5.422742	5.706443
C	5.663474	-6.163828	6.050749	C	5.492605	-6.238501	6.06473
H	5.003718	-7.024984	5.923487	H	4.992698	-7.20954	6.051047
H	5.421461	-5.423602	5.281584	H	5.009127	-5.597241	5.320257
H	5.439803	-5.698758	7.016881	H	5.322102	-5.773952	7.04121
C	9.169223	-9.737743	5.42472	C	9.429965	-9.118939	4.771244
H	8.857829	-10.376634	6.258036	H	9.612646	-9.735652	5.65834
H	10.246207	-9.864101	5.289858	H	10.380957	-9.014238	4.242467
H	8.66835	-10.111049	4.526321	H	8.738012	-9.669372	4.127964
C	10.554714	-4.970787	6.374355	C	10.129292	-4.24423	5.872071
H	10.470302	-4.151132	5.654695	H	9.722238	-3.3557	5.381175
H	11.546066	-5.418803	6.275706	H	11.115339	-4.456998	5.453031
H	10.478468	-4.527658	7.373061	H	10.255963	-3.992896	6.931175
C	5.186993	0.597436	1.700984	C	5.186168	0.129896	1.972127
C	5.990887	1.449888	0.932838	C	6.259713	0.597464	1.199999
C	5.655553	1.653094	-0.406724	C	6.076583	0.728665	-0.174787
H	6.274351	2.313654	-1.009728	H	6.900948	1.091863	-0.784358
C	4.557476	1.023562	-0.991175	C	4.86624	0.398891	-0.789405
C	3.77499	0.18117	-0.198698	C	3.820256	-0.064233	0.00731
H	2.907556	-0.307379	-0.637013	H	2.86922	-0.317165	-0.455138
C	4.06672	-0.039364	1.14605	C	3.956935	-0.199882	1.389938
C	7.181824	2.13914	1.54467	C	7.570426	0.955306	1.849157
H	7.776013	2.643528	0.779373	H	8.320188	1.212377	1.09795
H	7.821351	1.425646	2.071906	H	7.950292	0.124773	2.451376
H	6.870188	2.890362	2.279077	H	7.458308	1.812452	2.522246

C	4.228782	1.227735	-2.448569
H	4.727108	2.113643	-2.850094
H	3.151592	1.343672	-2.599528
H	4.550194	0.366478	-3.044467
C	3.197121	-0.925388	1.998447
H	3.748349	-1.800175	2.358174
H	2.325821	-1.272745	1.43866
H	2.845768	-0.389065	2.886254

C	4.706561	0.540405	-2.282076
H	4.973145	1.549202	-2.612332
H	3.678246	0.34199	-2.593623
H	5.360566	-0.158279	-2.814027
C	2.810583	-0.673021	2.244604
H	3.04268	-1.623237	2.73604
H	1.907393	-0.809948	1.646158
H	2.590576	0.048963	3.037932

uM06 singlet state

Atom	x	y	z
Cu	6.159964	-1.220455	6.106886
Cl	5.874849	-2.591118	4.371984
N	5.594208	0.917747	5.306769
N	6.07216	-0.041117	7.781602
N	7.275565	-2.449639	7.743839
N	7.946566	-4.200381	6.412692
H	7.502838	-3.665704	5.668392
N	5.664661	0.45215	3.057118
H	5.948967	-0.476938	3.361081
C	5.240815	1.265631	4.064435
C	4.47688	2.426209	3.812747
H	4.20389	2.685682	2.793532
C	4.080973	3.194242	4.885832
H	3.47579	4.082424	4.721401
C	4.443986	2.826696	6.18267
H	4.113701	3.409221	7.036422
C	5.211909	1.67986	6.338705
C	5.676691	1.232068	7.673418
C	5.740631	2.103275	8.760596
H	5.443159	3.141692	8.655646
C	6.232727	1.631416	9.967924
H	6.30681	2.29356	10.826055
C	6.660919	0.315968	10.060253
H	7.090327	-0.059088	10.983563
C	6.566994	-0.502676	8.935472
C	7.040528	-1.907774	8.945573
C	7.231309	-2.60267	10.132628
H	6.998426	-2.158257	11.094805
C	7.705808	-3.912999	10.049996
H	7.865421	-4.491373	10.956762
C	7.960728	-4.480476	8.820723

uM06 triplet state

Atom	x	y	z
Cu	5.896312	-1.051035	6.472702
Cl	4.842074	-2.54561	5.134601
N	5.396317	0.740413	5.558759
N	6.039379	0.10441	7.956487
N	6.897815	-2.304768	7.788846
N	7.415767	-4.00687	6.295025
H	6.725564	-3.581781	5.683351
N	5.463217	0.018431	3.349953
H	5.427769	-0.923881	3.726221
C	5.210812	1.012571	4.248025
C	4.797607	2.284069	3.818864
H	4.625277	2.457607	2.761324
C	4.607687	3.284808	4.760623
H	4.284039	4.272327	4.441098
C	4.839843	3.027899	6.101735
H	4.728254	3.806788	6.849687
C	5.241412	1.747726	6.478489
C	5.575776	1.381959	7.834354
C	5.498673	2.187239	8.959662
H	5.123872	3.204463	8.882097
C	5.910252	1.681817	10.197128
H	5.852959	2.303576	11.085437
C	6.408272	0.376037	10.285808
H	6.743544	-0.018767	11.241309
C	6.470161	-0.406028	9.145185
C	6.982548	-1.753999	9.042277
C	7.562696	-2.440367	10.10621
H	7.623261	-1.978768	11.086778
C	8.075534	-3.708073	9.880536
H	8.526378	-4.268211	10.695911
C	8.02389	-4.26099	8.610488

H	8.3246	-5.49996	8.725961	H	8.417597	-5.251273	8.403835
C	7.721691	-3.707873	7.66307	C	7.437349	-3.524001	7.568351
C	8.219199	-5.576903	6.165072	C	7.878482	-5.308682	5.950059
C	7.152868	-6.467905	5.97875	C	6.960077	-6.366275	5.863856
C	7.443406	-7.808132	5.7261	C	7.429129	-7.624409	5.494757
H	6.620151	-8.508735	5.579665	H	6.721143	-8.451425	5.421343
C	8.755738	-8.275808	5.666798	C	8.780153	-7.855218	5.229464
C	9.793836	-7.367038	5.873336	C	9.668974	-6.787997	5.341055
H	10.826059	-7.718532	5.839245	H	10.72808	-6.951878	5.138102
C	9.549208	-6.016444	6.118781	C	9.240866	-5.507753	5.695621
C	5.734907	-5.991331	6.062835	C	5.511134	-6.142752	6.171664
H	5.034641	-6.819766	5.918495	H	4.963785	-7.090031	6.189141
H	5.519488	-5.221809	5.310155	H	5.033625	-5.488	5.431623
H	5.523276	-5.536376	7.039841	H	5.383287	-5.651817	7.145423
C	9.047228	-9.716135	5.368077	C	9.253612	-9.223645	4.840067
H	8.209338	-10.362469	5.650082	H	9.080309	-9.949581	5.644008
H	9.941472	-10.062993	5.897357	H	10.323695	-9.228662	4.609618
H	9.228489	-9.869307	4.296471	H	8.716767	-9.594191	3.958613
C	10.679676	-5.056731	6.333397	C	10.214112	-4.374793	5.805528
H	10.655565	-4.241437	5.60096	H	9.916615	-3.529907	5.173427
H	11.645331	-5.564762	6.249038	H	11.219305	-4.690659	5.510327
H	10.630498	-4.587043	7.324048	H	10.267633	-3.99192	6.833325
C	5.258099	0.61849	1.703161	C	5.253375	0.172216	1.950288
C	6.013986	1.441631	0.856337	C	6.2514	0.77517	1.169049
C	5.601811	1.588721	-0.467148	C	6.028041	0.913849	-0.198594
H	6.183671	2.228238	-1.132587	H	6.798142	1.381436	-0.81411
C	4.472925	0.934835	-0.962295	C	4.852538	0.462279	-0.802047
C	3.737771	0.130609	-0.092604	C	3.882608	-0.133315	0.001199
H	2.843813	-0.375649	-0.459483	H	2.955278	-0.485602	-0.452351
C	4.107925	-0.035909	1.242056	C	4.058528	-0.280411	1.377964
C	7.233592	2.148554	1.364028	C	7.522293	1.262521	1.794062
H	7.725277	2.70588	0.560782	H	8.222553	1.618786	1.032436
H	7.957486	1.442099	1.786643	H	8.011248	0.469742	2.372151
H	6.987288	2.858098	2.164381	H	7.334279	2.088601	2.49276
C	4.075969	1.080979	-2.400802	C	4.649651	0.62106	-2.27928
H	4.242701	2.102091	-2.761525	H	4.678775	1.676977	-2.574674
H	3.021007	0.831175	-2.554646	H	3.687592	0.2091	-2.600145
H	4.666096	0.414882	-3.043146	H	5.439285	0.11256	-2.84569
C	3.290679	-0.883509	2.16852	C	2.992492	-0.899167	2.228877
H	3.861507	-1.745057	2.538784	H	3.320031	-1.853643	2.66065
H	2.39042	-1.254534	1.669246	H	2.084631	-1.085179	1.647053
H	2.98071	-0.317112	3.05704	H	2.732171	-0.250904	3.076024

uB3LYP singlet state

Atom	x	y	z
Cu	6.221305	-1.184028	6.073568
Cl	6.037727	-2.562561	4.279032
N	5.594109	0.965584	5.274848
N	6.186429	0.001065	7.760105
N	7.230013	-2.523303	7.772649
N	7.730898	-4.380649	6.497581
H	7.329064	-3.847566	5.730378
N	5.456767	0.46951	3.024693
H	5.740138	-0.465395	3.30709
C	5.167251	1.324202	4.049516
C	4.458723	2.533891	3.841991
H	4.123273	2.801023	2.847422
C	4.187105	3.334866	4.934878
H	3.624692	4.25471	4.805153
C	4.622557	2.954155	6.209459
H	4.387482	3.561564	7.073729
C	5.335946	1.760912	6.32673
C	5.872942	1.304056	7.640531
C	6.07206	2.197804	8.69986
H	5.84793	3.250388	8.582788
C	6.602401	1.722268	9.893978
H	6.783098	2.399513	10.722375
C	6.926464	0.374676	10.003885
H	7.375336	-0.007295	10.911912
C	6.703372	-0.46978	8.909561
C	7.056829	-1.917295	8.959166
C	7.209841	-2.585763	10.174227
H	7.024976	-2.092748	11.119767
C	7.582204	-3.934502	10.137595
H	7.706213	-4.489149	11.062945
C	7.777813	-4.566642	8.924337
H	8.055323	-5.612123	8.86907
C	7.577261	-3.823169	7.734642
C	8.106	-5.737156	6.255733
C	7.122824	-6.672565	5.876773
C	7.519139	-7.986869	5.606999
H	6.763693	-8.71082	5.309531
C	8.852858	-8.395452	5.718306
C	9.805656	-7.443402	6.096026
H	10.850263	-7.737252	6.171827
C	9.459892	-6.11319	6.360599

uB3LYP triplet state

Atom	x	y	z
Cu	5.829764	-1.044685	6.517233
Cl	4.746529	-2.549638	5.152415
N	5.364579	0.785161	5.58614
N	6.024542	0.124981	7.997469
N	6.837121	-2.325362	7.850375
N	7.25268	-4.088891	6.382534
H	6.526301	-3.685624	5.799464
N	5.305078	0.041117	3.376611
H	5.212804	-0.89258	3.763355
C	5.164637	1.065132	4.271046
C	4.840383	2.367598	3.842639
H	4.663425	2.549578	2.790626
C	4.731002	3.3845	4.785463
H	4.473828	4.390377	4.467624
C	4.955647	3.112109	6.12926
H	4.902707	3.89933	6.870793
C	5.281032	1.805418	6.508947
C	5.614872	1.426955	7.869528
C	5.586248	2.248033	8.991695
H	5.252561	3.276303	8.911196
C	5.996695	1.738641	10.232461
H	5.972508	2.3691	11.114276
C	6.456183	0.416693	10.324871
H	6.795878	0.025887	11.277248
C	6.475	-0.384178	9.187966
C	6.966266	-1.746473	9.094406
C	7.582687	-2.419044	10.155173
H	7.680394	-1.941094	11.121833
C	8.090118	-3.693987	9.937448
H	8.569404	-4.236602	10.746629
C	7.988462	-4.27659	8.678322
H	8.366323	-5.271678	8.482796
C	7.355264	-3.564507	7.64057
C	7.784561	-5.355464	5.988815
C	6.920725	-6.460382	5.852064
C	7.455931	-7.676877	5.415969
H	6.791715	-8.53109	5.304536
C	8.817829	-7.826581	5.13051
C	9.649228	-6.711385	5.277051
H	10.707996	-6.803226	5.045285
C	9.157674	-5.469316	5.695303

C	5.671492	-6.270799	5.766441
H	5.047745	-7.135284	5.525105
H	5.517912	-5.512284	4.991291
H	5.307143	-5.837799	6.704704
C	9.248963	-9.830425	5.458979
H	9.180278	-10.431229	6.374683
H	10.280294	-9.902193	5.101009
H	8.595711	-10.297379	4.715908
C	10.523265	-5.10858	6.734071
H	10.454794	-4.209596	6.113221
H	11.520947	-5.538072	6.613097
H	10.424682	-4.78112	7.775773
C	5.101165	0.684197	1.658461
C	5.875648	1.55667	0.867703
C	5.522681	1.731468	-0.475008
H	6.120228	2.400768	-1.090117
C	4.43979	1.057131	-1.050056
C	3.700465	0.186042	-0.242868
H	2.858263	-0.351856	-0.672437
C	4.00574	-0.009727	1.108646
C	7.070063	2.2785	1.443559
H	7.632466	2.786176	0.655946
H	7.742498	1.584376	1.957805
H	6.771576	3.033019	2.180915
C	4.066885	1.280338	-2.497267
H	3.40148	2.146183	-2.605571
H	3.543489	0.414504	-2.913139
H	4.950649	1.473826	-3.112882
C	3.175489	-0.945411	1.954406
H	3.759921	-1.805082	2.30053
H	2.319626	-1.322095	1.388557
H	2.798382	-0.441579	2.851082

C	5.449424	-6.339857	6.169534
H	4.959901	-7.315417	6.113272
H	4.9369	-5.664761	5.47524
H	5.291675	-5.935198	7.175051
C	9.376566	-9.162038	4.697487
H	9.615014	-9.790738	5.564574
H	10.297638	-9.041656	4.119814
H	8.658709	-9.716272	4.085143
C	10.08349	-4.282877	5.812776
H	9.685666	-3.414587	5.27754
H	11.069388	-4.518935	5.40456
H	10.216832	-3.976814	6.85691
C	5.171514	0.183234	1.960782
C	6.250112	0.69303	1.211511
C	6.109023	0.792688	-0.177337
H	6.940287	1.182535	-0.760612
C	4.941797	0.389638	-0.834699
C	3.89444	-0.126369	-0.063498
H	2.979853	-0.449471	-0.555788
C	3.98282	-0.231621	1.328748
C	7.53691	1.11291	1.879739
H	8.299638	1.353335	1.134852
H	7.924372	0.320478	2.528377
H	7.393962	1.997216	2.511499
C	4.806592	0.528558	-2.333161
H	4.350075	1.489649	-2.601531
H	4.172666	-0.258471	-2.752473
H	5.781015	0.482991	-2.828376
C	2.825812	-0.77763	2.131065
H	3.080481	-1.72496	2.619
H	1.958104	-0.951677	1.489802
H	2.530343	-0.084372	2.926052

uM06L singlet state

Atom	x	y	z
Cu	5.975199	-1.22687	6.237896
Cl	5.290916	-2.718639	4.691035
N	5.462202	0.813031	5.417742
N	5.969349	-0.018117	7.88368
N	7.183903	-2.365136	7.748517
N	7.766898	-4.113488	6.363668
H	7.227457	-3.600007	5.672136
N	5.453766	0.230552	3.183619

H	5.585234	-0.722837	3.510431
C	5.106558	1.12661	4.156136
C	4.419589	2.320339	3.853914
H	4.151342	2.539238	2.82548
C	4.076874	3.169245	4.887621
H	3.522453	4.079638	4.679505
C	4.427437	2.844484	6.197368
H	4.146112	3.487185	7.023631
C	5.129711	1.662876	6.415765
C	5.612958	1.272183	7.750952
C	5.764378	2.175177	8.804132
H	5.485033	3.21629	8.683323
C	6.320205	1.728876	9.997265
H	6.459412	2.416038	10.825784
C	6.746537	0.41066	10.100728
H	7.240637	0.059979	11.000473
C	6.566186	-0.443691	9.011931
C	7.057299	-1.831233	8.983536
C	7.388546	-2.526162	10.142915
H	7.238551	-2.083277	11.1208
C	7.900743	-3.817138	10.012155
H	8.176246	-4.387292	10.894405
C	8.046997	-4.376288	8.758056
H	8.449575	-5.375061	8.622931
C	7.656213	-3.622477	7.631212
C	8.032929	-5.490902	6.091725
C	7.004479	-6.439504	6.21291
C	7.298698	-7.774407	5.930883
H	6.507428	-8.517367	6.023219
C	8.576421	-8.180637	5.53887
C	9.578395	-7.212988	5.440747
H	10.583469	-7.513096	5.146998
C	9.329446	-5.866515	5.712764
C	5.63518	-6.02316	6.650118
H	4.940477	-6.865878	6.630563
H	5.233053	-5.225437	6.015653
H	5.647479	-5.622944	7.671452
C	8.857902	-9.615234	5.210073
H	9.904679	-9.874071	5.390648
H	8.654267	-9.827818	4.154206
H	8.232272	-10.294218	5.795822
C	10.418694	-4.844233	5.617037
H	10.155218	-4.038647	4.924406

H	11.354581	-5.29461	5.278297
H	10.605709	-4.364681	6.584413
C	5.25409	0.449661	1.796286
C	6.029775	1.414028	1.128146
C	5.829329	1.595743	-0.241552
H	6.434234	2.336827	-0.763051
C	4.899611	0.843476	-0.961155
C	4.154084	-0.113989	-0.270289
H	3.420741	-0.711576	-0.810669
C	4.305348	-0.320475	1.100991
C	7.055364	2.221716	1.859239
H	7.758749	2.685382	1.163791
H	7.618386	1.606302	2.567924
H	6.598392	3.027348	2.448017
C	4.690956	1.073488	-2.42709
H	3.913256	1.825066	-2.606546
H	4.373566	0.160906	-2.939026
H	5.601025	1.436928	-2.912436
C	3.471703	-1.331576	1.821846
H	4.068857	-2.174283	2.188327
H	2.689266	-1.731088	1.172537
H	2.995573	-0.898027	2.708967

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