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# Synthesis, Crystallographic and Spectroscopic Characterizations, and Theoretical Elucidation of an Elusive Aminyl Radical Containing $Cu^{II}$-Aminyl-Iminosemiquinone Complex‡

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**Materials:**

Chemicals and solvents were purchased from commercial sources as supplied. 2-picolylamine, 2-nitrobenzyl bromide, sodium borohydride, Pd-C, 3,5–di–*tert*–butylcatechol were bought from Sigma–Aldrich. Solvents were obtained from Merck (India). Mass spectra were measured in HPLC grade acetonitrile and methanol solvent**.**

**Physical methods:**

X-ray crystallographic data were collected at 100 K using Super Nova, Single source at offset, Eos diffractometer. The data refinement and cell reductions were carried out by CrysAlisPro.[1] Structures were solved by direct methods using SHELXS–97.[2] SQUEEZE operations were performed using WinGX programme.[3] All the non–hydrogen atoms were refined anisotropically. IR spectra were recorded on a Perkin Elmer Instrument from 4000 $cm^{-1}$ to 400 $cm^{-1}$ at normal temperature as KBr pellets. $^{1}H$–, and $^{13}C$–NMR spectra of the ligand were recorded in BRUKER 600 MHz NMR machines. Variable-temperature magnetic susceptibility measurements were performed using a superconducting quantum interference device (SQUID) magnetometer at 1 T for complex **1**. Simulations of the experimentally obtained magnetic measurements were done using the julX program developed by Dr. E. Bill. Mass spectral (MS) data were acquired from quadrupole time-of-flight (QTOF)-MS spectrometer. UV–vis/NIR spectra, and spectroelectrochemical data were recorded on a Perkin Elmer Lamda 750, by preparing a known concentration of the samples in HPLC Grade $CH_2Cl_2$ (DCM) at room temperature (25 °C) using a cuvette of 1 cm width. Cyclic voltammograms (CVs) of the complex were being recorded in DCM solutions containing 0.10 M $[(^{n}Bu)_4N]ClO_4$ as supporting electrolyte at a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. The experiments were performed at different scan rates. Ferrocene was used as an internal standard, and potentials are referenced *versus* the ferrocenium/ferrocene ($Fc^{+}$/Fc) couple. BASi SEC-C thin layer quartz glass spectroelectrochemical cell kit (light path length of 1 mm) with platinum gauze working electrode, and SEC-C platinum counter electrode were taken for the fixed potential spectroelectrochemistry measurements in DCM under argon blanketing atmosphere. The DCM solvent was dried and saturated with argon gas for 45 minutes before using for the measurements. After the electrochemical process; the respective samples were collected in EPR tubes, kept under argon atmosphere, and X-band EPR were recorded immediately. In case of $\mathbf{1}^{2+}$; the species was isolated as solid powder by oxidizing complex **1** with 2.02 equivalent amounts of $AgSbF_6$.

**Computational Methodologies:**

The Density Functional Theory (DFT) based calculations were performed using Gaussian 09[4] program package. Becke's three–parameter[5,6] hybrid exchange functional with Lee-Yang-Parr gradient-corrected correlation (B3LYP functional). Subsequently, the 6-31G+(d,p) basis sets are used for the lighter atoms. Whereas, ECP (electrostatic core potential) based LANL2DZ,[7] basis sets is incorporated to define the Cu metal center. ECP approaches allow chemically inactive

core electrons to be treated as an averaged potential rather than actual particle. This reduces the computational cost and takes care of relativistic effects. The outer electrons are represented by double-zeta atomic orbitals. Studies of TM containing systems have widely utilized density functional methods with the LANL2DZ basis set for the transition metal (s) and an all-electron Pople type basis set for all other atoms.[8] Structures of transition metal complexes have been successfully predicted by methodologies using B3LYP and the LANL2DZ basis set.[9] All calculations were performed considering DCM solvent environment within the Integral Equation Formalism - Polarizable Continuum Model (IEF-PCM).[10] Chemcraft[11] software was used to visualize all the optimized structures at an isovalue of 0.02.

**Broken symmetry approach:**

The broken symmetry approach, developed by Noodleman et al., is a method used to calculate antiferromagnetic spin states. It has been widely used to model weakly coupled polymetallic systems and describe their structural and magnetic properties.[12] In the broken symmetry approach, the symmetry elements connecting the unpaired electron centres are removed and an asymmetry in the initial spin density is imposed by the unpaired electron centres having opposite spins. A spin unrestricted calculation is performed, allowing individual electrons to localise on one centre or the other, but only if this is energetically favoured over delocalisation. This means that α and β electrons are able to localize on opposite sides of the molecule, giving the antiferromagnetic state. Through use of the broken symmetry approach, a range of antiferromagnetic coupling modes are possible, from weak antiferromagnetic coupling to strong metal-metal bonding modes.[13] The broken symmetry state contains a weighted average of the Ms = 0 components of all spin states; it is not a pure antiferromagnetic spin singlet. The broken symmetry approach has been used to approximate the antiferromagnetic state of many transition metal dimers.[14] As the calculation of magnetic properties is highly sensitive and DFT methods are not the gold standard (for such calculations), we have incorporated minor changes to the computational methodologies to achieve some better qualitative correlation to the experiment. The systems considered for the present study are relatively large (in terms of number of atoms) and multireference electron correlation methods such as CASPT2, CASSCF, etc. are not feasible with our computational resources. Subsequently, calculations are performed at the same level of theory i.e., B3LYP however, we have introduced the higher-order (all-electron cc-PVTZ) basis sets for improved accuracy in the calculations.

**Calculating the exchange coupling constant:**

A number of different equations have been proposed to determine the exchange coupling constant of a dimer from the calculated broken-symmetry and high-spin states. The appropriateness of each approximation is a subject of debate in the literature.[15]
Yamaguchi proposed an excellent formulation, which covers the range of coupling situations:[16]

$$J = -\frac{E_{HS} - E_{BS}}{\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{BS}}$$

Here, $E_{HS}$ and $E_{BS}$ are the energies of the system in high-spin and broken symmetry states. $S^2$ are the total spin angular momentum expectation values for the high-spin and broken-symmetry states, respectively. The equation proposed by Yamaguchi will be used in the present study to calculate the exchange coupling constant as it is suitable for a range of coupling situations.

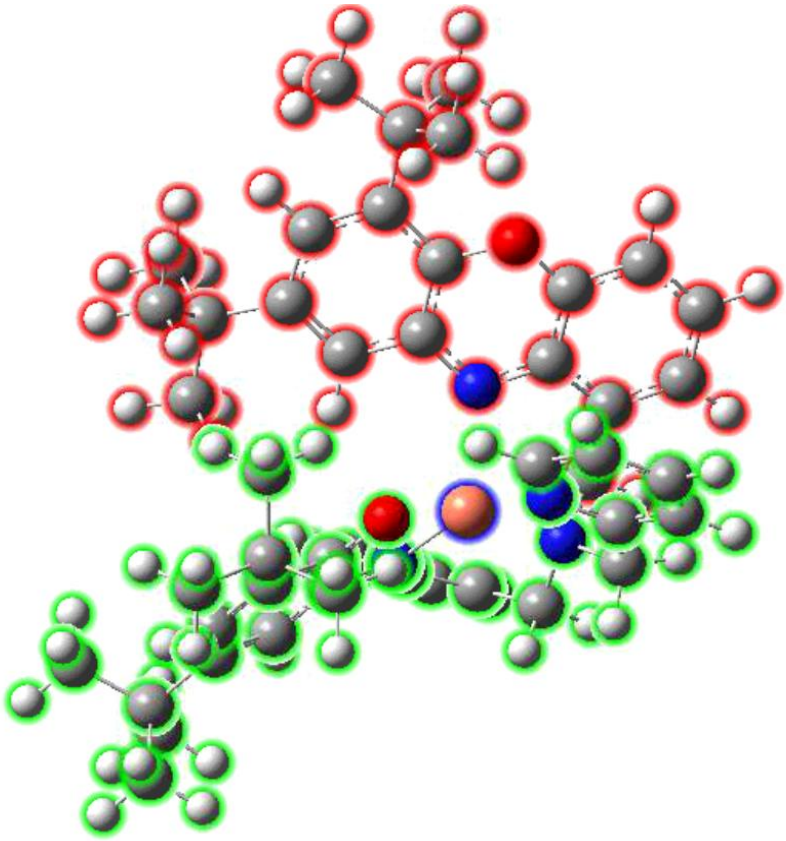


**Figure S1**. Fragments of the complex **1** defined using the atoms group editor in Gaussview 5.0

The first set of calculations were performed with a spin multiplicity of four in order to model the ferromagnetically coupled complex. The spin multiplicity for a molecule is given by the equation 2S+1 where S is the total spin. In the ferromagnetic state complex 1 has three unpaired electrons would result in a total spin of 3 × 1/2 = 3/2. The spin multiplicity would then be 2S+1 = 4 (quartet). Calculations were then performed with the spin multiplicity of two in order to model the antiferromagnetically coupled complex. In the antiferromagnetic state, it is assumed that the two unpaired electrons present in the ligands are weakly coupled due to opposite spin arrangements. So, the spin density at the metal center is intake, resulting an overall doublet spin multiplicity for the complex.

The value of $<S^2>$ (spin-squared operator) was monitored throughout each of the calculations in order to ensure that the calculated system had the correct spin distribution. The generalised spin-squared operator equation for the spin of a multi-electron system is as follows:

$$\hat{\mathbf{S}}^2\boldsymbol{\Psi} = S(S+1)\hbar^2\boldsymbol{\Psi}$$

Based on this equation, the eigenvalue of $<S^2>$ for a quartet spin state would be 3/2(3/2+1) = 3.75. For a doublet spin state the eigenvalue of $<S^2>$ would be 1/2(1/2+1) = 0.75. The ferromagnetic calculation was monitored to ensure that the value of $<S^2>$ was consistent (3.750552) through out the run.

If the value of $<S^2>$ is significantly greater than S(S+1), it is common practice to consider the calculation to be "badly spin contaminated".[13] However, for the broken symmetry state, used to model the antiferromagnetic state, it is required that the value of $<S^2>$ should be greater than the correct value. It is important to note that the computed $<S^2>$ value of broken symmetry doublet state for complex **1** is found to be 0.860419, which is significantly higher than the $<S^2>$ value expected for a doublet state (0.75). This higher value of $<S^2>$ represents the "variational adjustment of neutral and ionic components" that is required for the correct result to be achieved.[13]

The energies of the computationally optimised ferromagnetic and antiferromagnetic complexes were compared to determine the most energetically favourable structure of the complex. The antiferromagnetic (broken symmetry, doublet) complex was lower in energy than the ferromagnetic (high spin, quartet) complex by $1.26 \times 10^{-3}$ Hartrees (3.30 $kJmol^{-1}$). This suggested that antiferromagnetic coupling between the two ligand centres could be energetically favourable.

The energy difference between the antiferromagnetic and ferromagnetic structures was close to kT at room temperature (2.48 kJ $mol^{-1}$) which suggests that the ferromagnetic and antiferromagnetic structures will both be present at room temperature in approximately. At lower temperatures the ferromagnetic structure will dominate. Due to the small difference in the energies of the calculated structures, if a different functional or basis set was used the results may differ.

The energy difference between the two structures was used to calculate the value of the exchange coupling using the equation proposed by Yamaguchi.

$$J = -\frac{E_{HS} - E_{BS}}{\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{BS}}$$

Here, $E_{HS}$–$E_{BS}$ = 1.26 x $10^{-3}$ Hartree = 276.53803 $cm^{-1}$

$$J = -\frac{276.53803cm-1}{3.750552-0.860419}$$
$$J = -\frac{276.53803cm-1}{2.890133}$$
$$J = -95.68cm-1$$

The calculated exchange coupling constant of -95.68 $cm^{-1}$ is consistent with antiferromagnetic coupling.

**Experimental Procedures**

**Synthesis of ligand $H_4L_{py}^{(AP)}$**: To a suspension of (**I**) (0.680 g, 2.14 mmol) in hexane (25 mL), 3,5-di-*tert*-butylcatechol (0.950 g, 4.28 mmol) was added. $Et_3N$ (0.05 mL) was added in it and the reaction mixture was refluxed under air for 48 h. After that the solution was further stirred at room temperature (25 °C) for 48 h. The solvent was evaporated and dried under vacuum. The oily residue was purified by column chromatography on silica gel using 2% ethyl acetate hexane mixture. The product was obtained as light green solid. Yield: 0.892 g, 57 %. FTIR (KBr pellet, $cm^{-1}$): 3484, 3404, 3330, 3278, 3048, 2954, 2906, 2818, 2798, 2713, 1589, 1504, 1480, 1465, 1446, 1427, 1390, 1362, 1318, 1308, 1294, 1259, 1222, 1200, 1151, 1118, 1096, 1050, 1024, 1003, 974, 930, 911, 881, 822, 805, 751, 654, 629. ESI-MS (+) *m/z* for $[C_{48}H_{62}N_4O_2 + H]^+$: calcd, 727.4945; found, 727.5096. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.0 Hz, 1H), 7.61 (dd, *J* = 6.0 Hz, 1H), 7.58 (s, 2H), 7.17 (t, *J* = 9.0 Hz, 3H), 7.10 (t, *J* = 9.0 Hz, 1H), 7.04-7.01 (m, 4H), 6.76 (d, *J* = 3.0 Hz, 2H), 6.71 (t, *J* = 12.0 Hz, 2H), 6.56 (s, 2H), 6.47 (d, *J* = 12.0 Hz, 2H), 3.81 (s, 4H), 3.79 (s, 2H), 1.31 (s, 18H), 1.13 (s, 18H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 158.17, 149.96, 148.57, 146.59, 141.33, 136.99, 135.32, 131.19, 128.86, 128.51, 123.91, 122.57, 122.32, 121.08, 120.87, 118.11, 114.07, 59.47, 59.01, 34.90, 34.18, 31.60, 29.57.

**Synthesis of Complex 1, $[C_{48}H_{57}N_4O_6CuCl_1]$:** To a continuous stirring solution of $H_4L_{py}$ (0.110 g, 0.15 mmol) in acetonitrile (5 mL), $Cu(ClO_4)_2 \bullet 6H_2O$ (0.054 g, 0.15 mmol) was added. After the addition of $Et_3N$ (0.09 mL), the colour of the solution changed into reddish brown. The mixture was further stirred for 3 hrs at room temperature (25 °C). No precipitate was observed. The solution was filtered and then solvent was removed completely. An oily residue appeared which was dissolved in dichloromethane (20 mL) and then tetrabutylammonium perchlorate (0.110 g, 0.315 mmol) was added into the solution. The resulted solution was stirred for 15 min and then filtered. To the filtrate, methanol (5 mL) was added and the solution of the solvent mixture was kept for solvent evaporation. After 3 days, pink crystals were appeared which were suitable for single crystal X-ray diffraction measurement. Yield: 0.066 g, 47%. FTIR (KBr pellet, $cm^{-1}$): 3426, 3060, 2954, 2906, 2869, 1636, 1608, 1582, 1567, 1548, 1522, 1478, 1460, 1435, 1385, 1364, 1333, 1316, 1286, 1259, 1236, 1203, 1179, 1108, 1097, 1048, 1031, 993, 969, 949, 910, 872, 859, 837, 785, 758, 745, 735, 691, 649, 623, 603, 593, 529, 510, 490, 413. UV-vis/NIR ($CH_3OH$) $\lambda_{max}$, nm ($\varepsilon$, $M^{-1}cm^{-1}$): 900(2700), 528(4860), 504(5000), 385(11600). ESI-MS (+) *m/z*

for $[C_{48}H_{57}N_4O_2Cu]^+$: calcd, 784.3877; found, 784.3863. Anal. Calcd for $C_{48}H_{57}N_4O_6CuCl_1 \bullet H_2O$: C, 62.65; H, 6.69; N, 6.09. Found: C, 62.87; H, 6.32; N, 6.06.

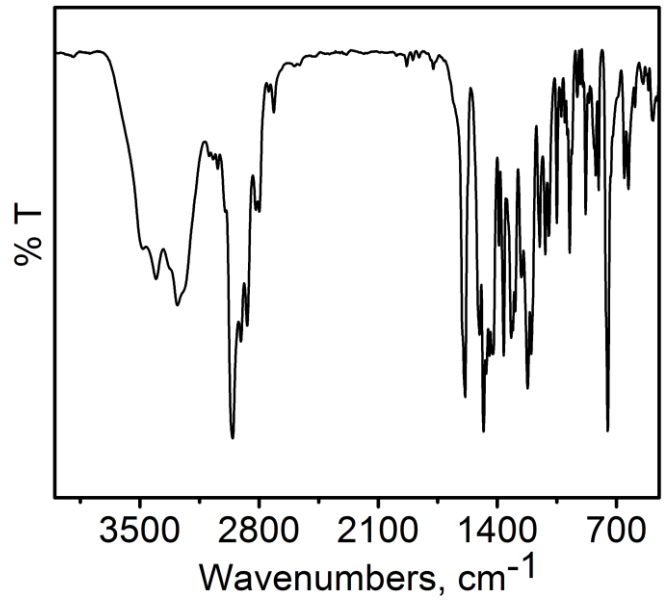



**Figure S2**. FTIR plot of $H_4L_{py}^{(AP)}$.

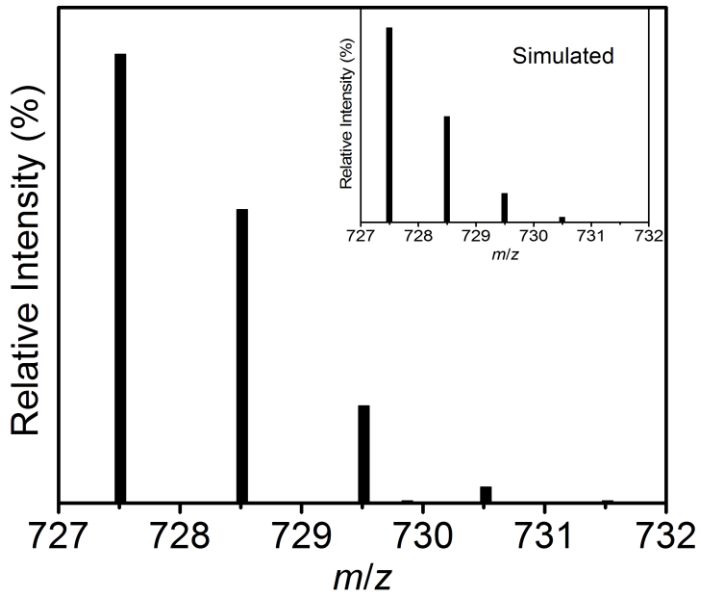



**Figure S3**. Experimental and simulated mass spectra for (A) $H_4L_{py}^{(AP)}$ + H = $[C_{48}H_{62}N_4O_2+H]^+$ have been shown.

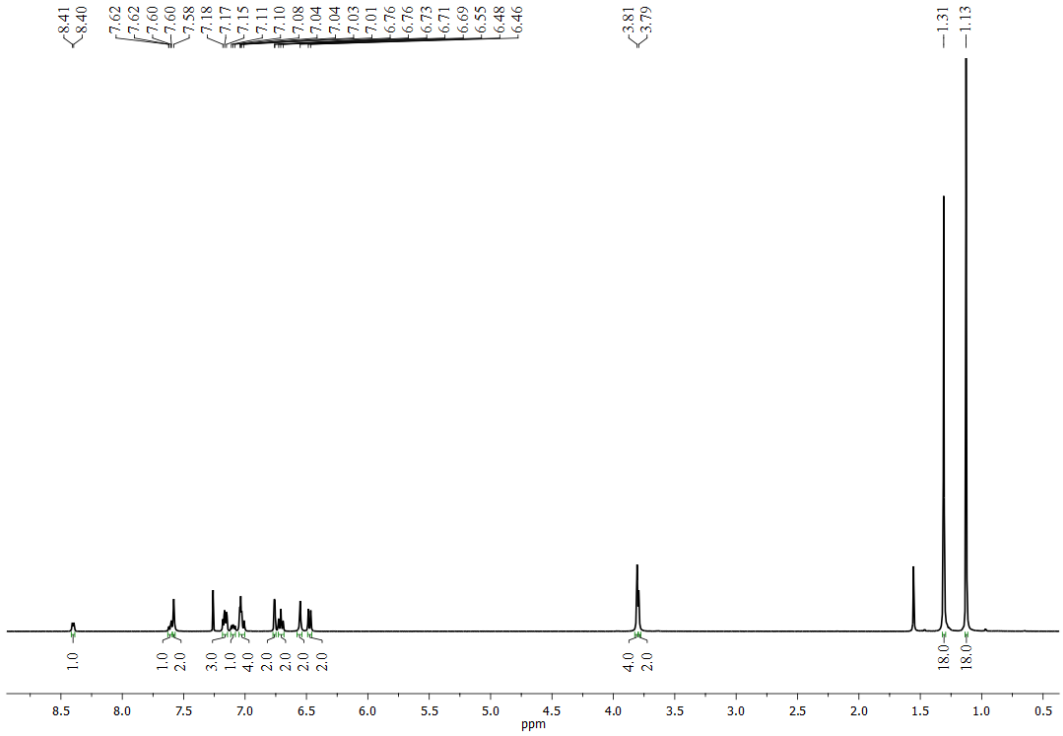



**Figure S4**. $^{1}$H-NMR spectrum of $H_4L_{py}^{(AP)}$ in $CDCl_3$.

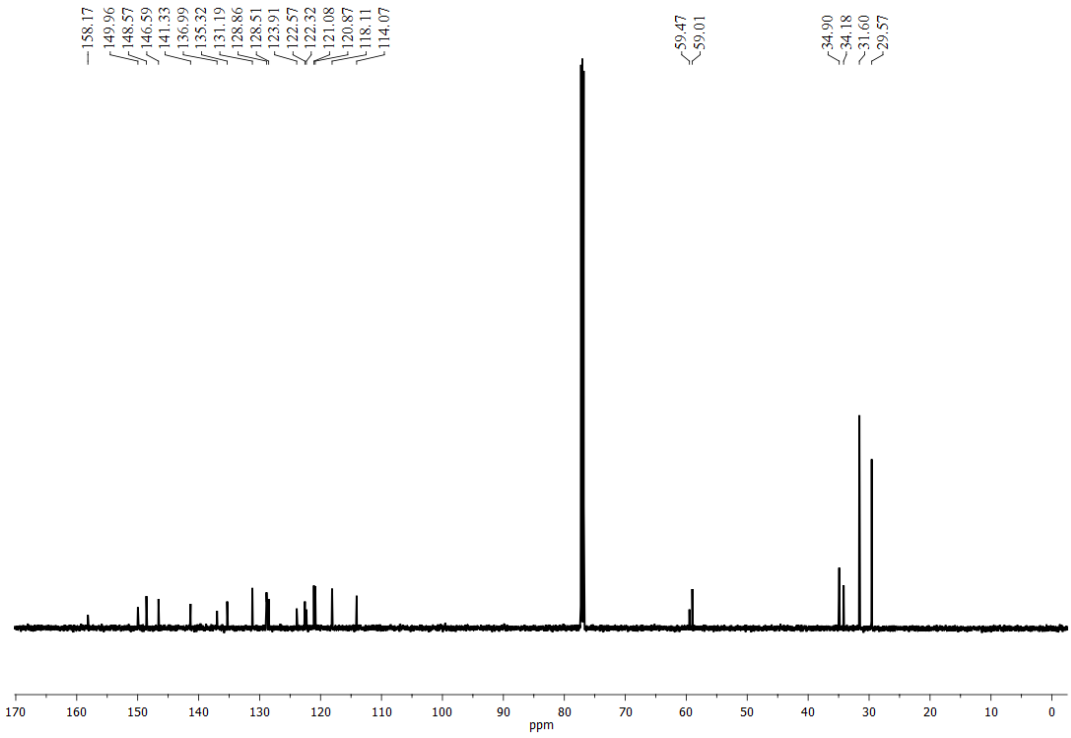


**Figure S5**. $^{13}$C-NMR spectrum of $H_4L_{py}^{(AP)}$ in $CDCl_3$.

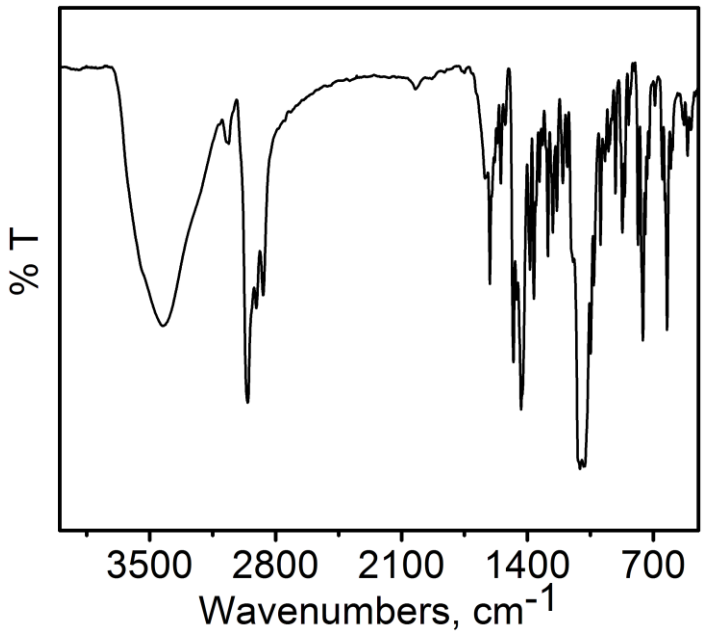



**Figure S6**. FTIR plot of complex **1**.

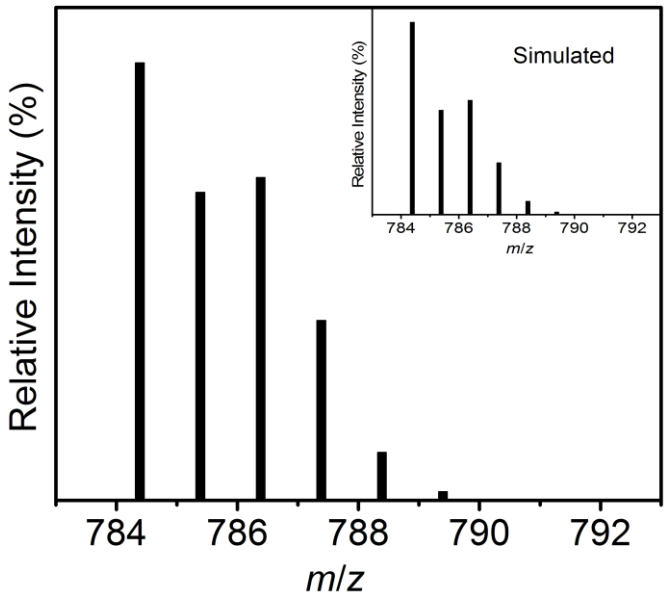



**Figure S7**. Experimental and simulated mass spectra for complex **1** = $[C_{48}H_{57}N_4O_2Cu]^+$ have been shown.

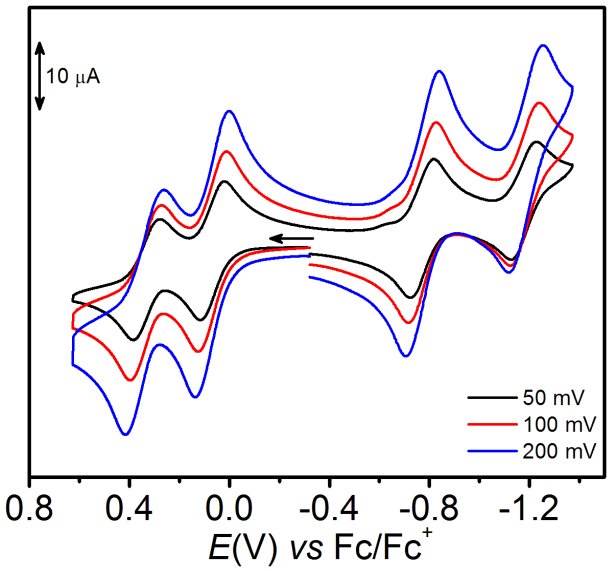



**Figure S8**. Cyclic voltammograms of complex **1** at 50, 100, 200 mV/s rates.

**Table S1**. Oxidation- and reduction-potentials of complex **1**.

| | |
|---|---|
| $E_{1/2}^{ox1}(\Delta E_p)$ | 0.068 V(108 mV) |
| $E_{1/2}^{ox2}(\Delta E_p)$ | 0.335 V(110 mV) |
| $E_{1/2}^{red1}(\Delta E_p)$ | -0.769 V(110 mV) |
| $E_{1/2}^{red2}(\Delta E_p)$ | -1.181 V(84 mV) |

$E^0$ values recorded at scan rates of 100 mV/s and referenced to the $Fc/Fc^+$ couple.

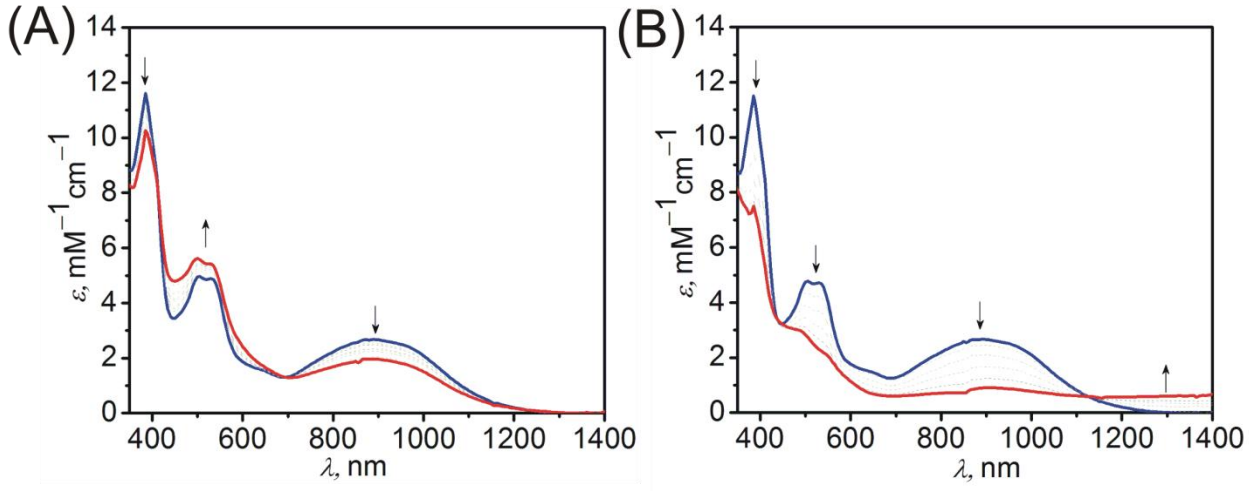



**Figure S9**. UV-Vis-NIR spectra changes of complex **1** during fixed potential coulometric one-electron (A) oxidation and (B) reduction.

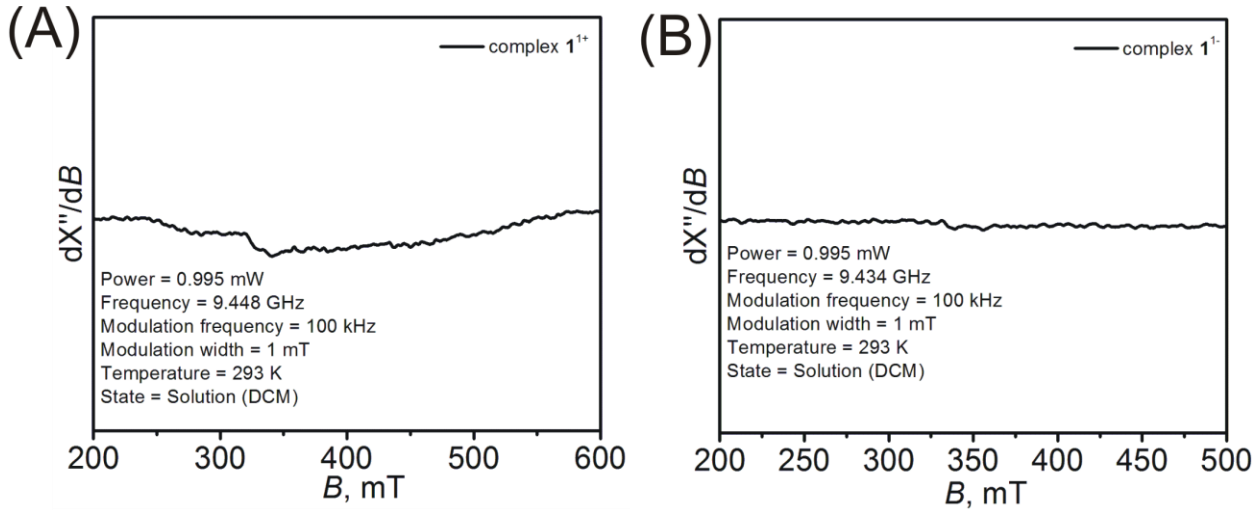



**Figure S10**. EPR Spectra of complex **1** after electrochemical one-electron: (C) oxidation (*i.e.***1**$^{1+}$) and (B) reduction (*i.e.***1**$^{1-}$).

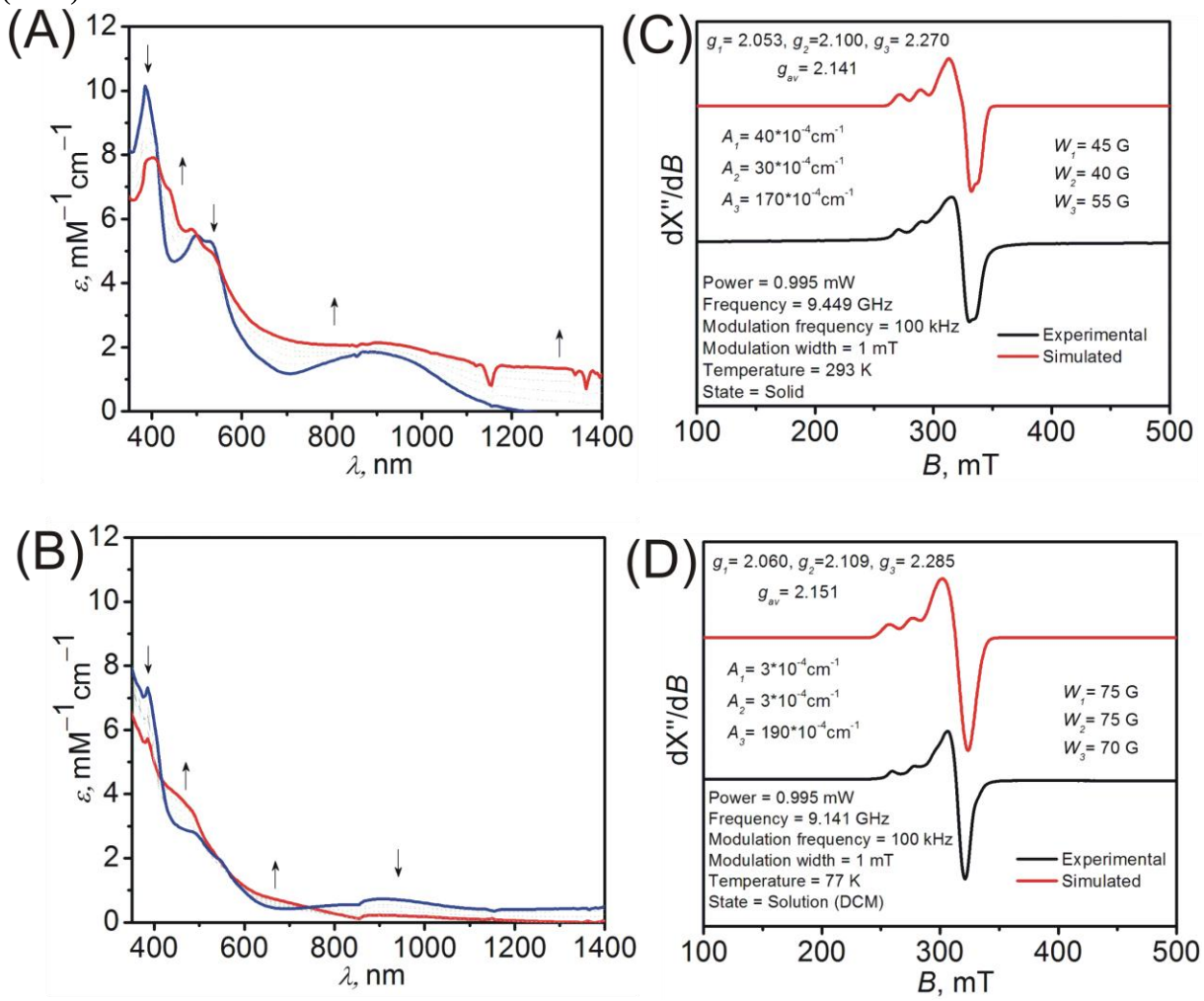
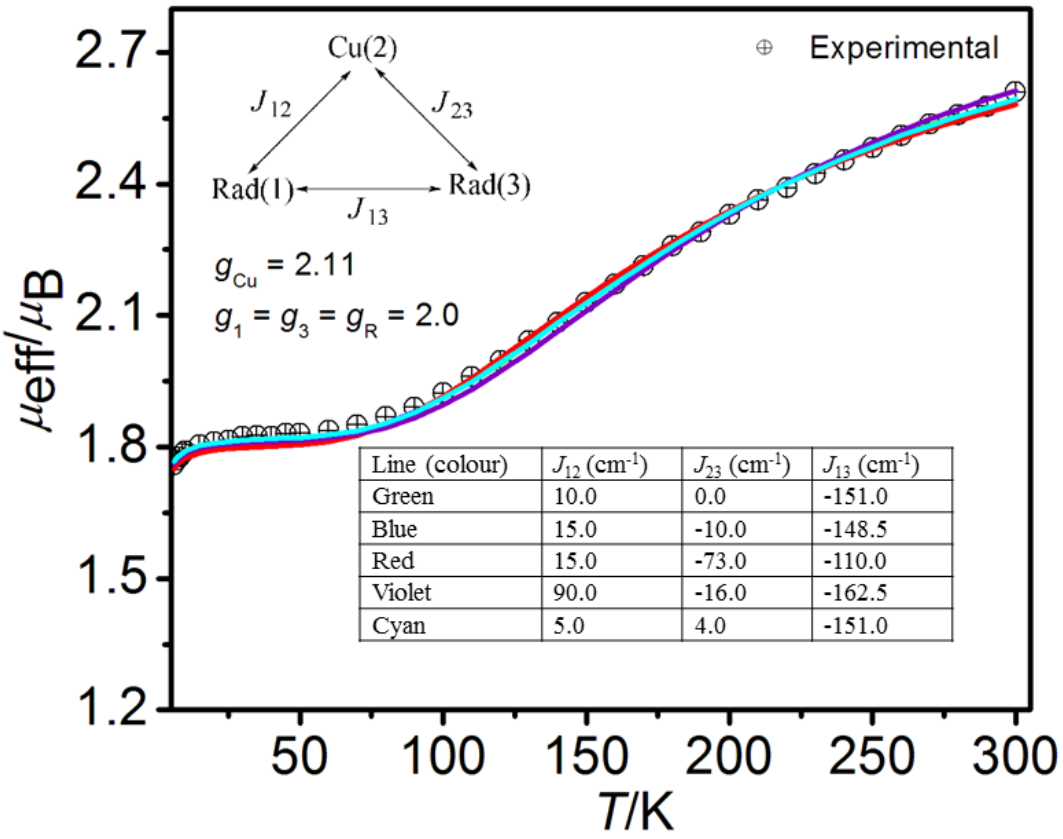



**Figure S11**. UV-Vis/NIR spectra changes of complex **1** during fixed potential coulometric 2$^{nd}$-one-electron (A) oxidation and (B) reduction; the corresponding EPR spectra for the (C) oxidation and (B) reduction.




| Line (colour) | $J_{12}$ (cm$^{-1}$) | $J_{23}$ (cm$^{-1}$) | $J_{13}$ (cm$^{-1}$) |
|---|---|---|---|
| Green | 10.0 | 0.0 | -151.0 |
| Blue | 15.0 | -10.0 | -148.5 |
| Red | 15.0 | -73.0 | -110.0 |
| Violet | 90.0 | -16.0 | -162.5 |
| Cyan | 5.0 | 4.0 | -151.0 |

**Figure S12**. Experimental and simulated $\mu_{eff}$ *vs. T* plots for complex **1** with the values given in the inset table.

**Table S3:** Crystallographic parameters and refinement data for complex **1**.

| | |
|---|---|
| Empirical formula | $C_{48}H_{57}CuN_4O_2,Cl_1O_4$ |
| Formula weight | 884.97 |
| CCDC Number | 2015612 |
| Crystal habit, colour | Block, pink |
| Crystal size, $mm^3$ | $0.35 \times 0.32 \times 0.30$ |
| Temperature, $T$ | 100(2) |
| Wavelength, $\lambda$ (Å) | 0.71073 |
| Crystal system | triclinic |
| Space group | 'P -1' |
| Unit cell dimensions | $a$ = 11.1397(5) Å<br>$b$ = 15.3727(9) Å<br>$c$ = 15.8265(10) Å<br>$\alpha$ = 63.174(6)°, $\beta$ = 76.983(5)°<br>$\gamma$ = 82.077(4)°, |
| Volume, $V$ ($Å^3$) | 2354.4(2) |
| $Z$ | 2 |
| Calculated density, $Mg \cdot m^{-3}$ | 1.248 |
| Absorption coefficient, $\mu$ ($mm^{-1}$) | 0.571 |
| $F$(000) | 934 |
| $\theta$ range for data collection | 2.35° to 25.00° |
| Limiting indices | $-13 \le h \le 13$, $-18 \le k \le 14$,<br>$-18 \le l \le 18$ |
| Reflection collected/unique | 15828/8283 [$R$(int)= 0.0296] |
| Completeness to $\theta$ | 99.9% ($\theta$ = 25.00°) |
| Max. and min. transmission | 0.854/0.819 |
| Refinement method | 'SHELXL–97(Sheldrick, 1997)' |
| Data/restraints/parameters | 8283/0/553 |
| Goodness–of–fit on $F^2$ | 1.048 |
| Final $R$ indices [$I$>2sigma($I$)] | $R$1 = 0.0549, $wR$2 = 0.1447 |
| $R$ indices (all data) | $R$1 = 0.0640, $wR$2 = 0.1512 |
| Largest diff. peak and hole | 1.117 and -1.045 $e \cdot Å^{-3}$ |

**Table S4:** Selected bond distances (Å) and bond angles (°) for complex **1**.

| | Complex **1** | | Complex **1** |
|---|---|---|---|
| Cu1–N1 | 1.934(3) | C5–C6 | 1.367(4) |
| Cu1–N2 | 2.037(3) | C6–C1 | 1.418(4) |
| Cu1–N3 | 1.977(3) | C35–C36 | 1.412(4) |
| Cu1–N4 | 2.329(3) | C36–C37 | 1.401(5) |
| Cu1–O1 | 1.940(2) | C37–C38 | 1.383(5) |
| C1–N1 | 1.355(4) | C38–C39 | 1.416(5) |
| C15–N1 | 1.403(4) | C39–C40 | 1.370(4) |
| C34–N4 | 1.374(4) | C40–C35 | 1.403(4) |
| C35–N4 | 1.372(4) | C29–C30 | 1.385(4) |
| C2–O1 | 1.290(4) | C30–C31 | 1.401(5) |
| C33–O2 | 1.367(4) | C31–C32 | 1.384(5) |
| C36–O2 | 1.383(4) | C32–C33 | 1.385(5) |
| C1–C2 | 1.458(4) | C33–C34 | 1.410(4) |
| C2–C3 | 1.440(4) | C34–C29 | 1.410(4) |
| C3–C4 | 1.369(4) | | |
| | | | |
| N1–Cu1–O1 | 84.09(9) | N3–Cu1–N2 | 83.86(10) |
| N1–Cu1–N3 | 165.35(11) | N1–Cu1–N4 | 98.08(10) |
| O1–Cu1–N3 | 93.12(10) | O1–Cu1–N4 | 100.29(9) |
| N1–Cu1–N2 | 96.31(10) | N3–Cu1–N4 | 96.57(10) |
| O1–Cu1–N2 | 169.53(10) | N2–Cu1–N4 | 90.03(10) |

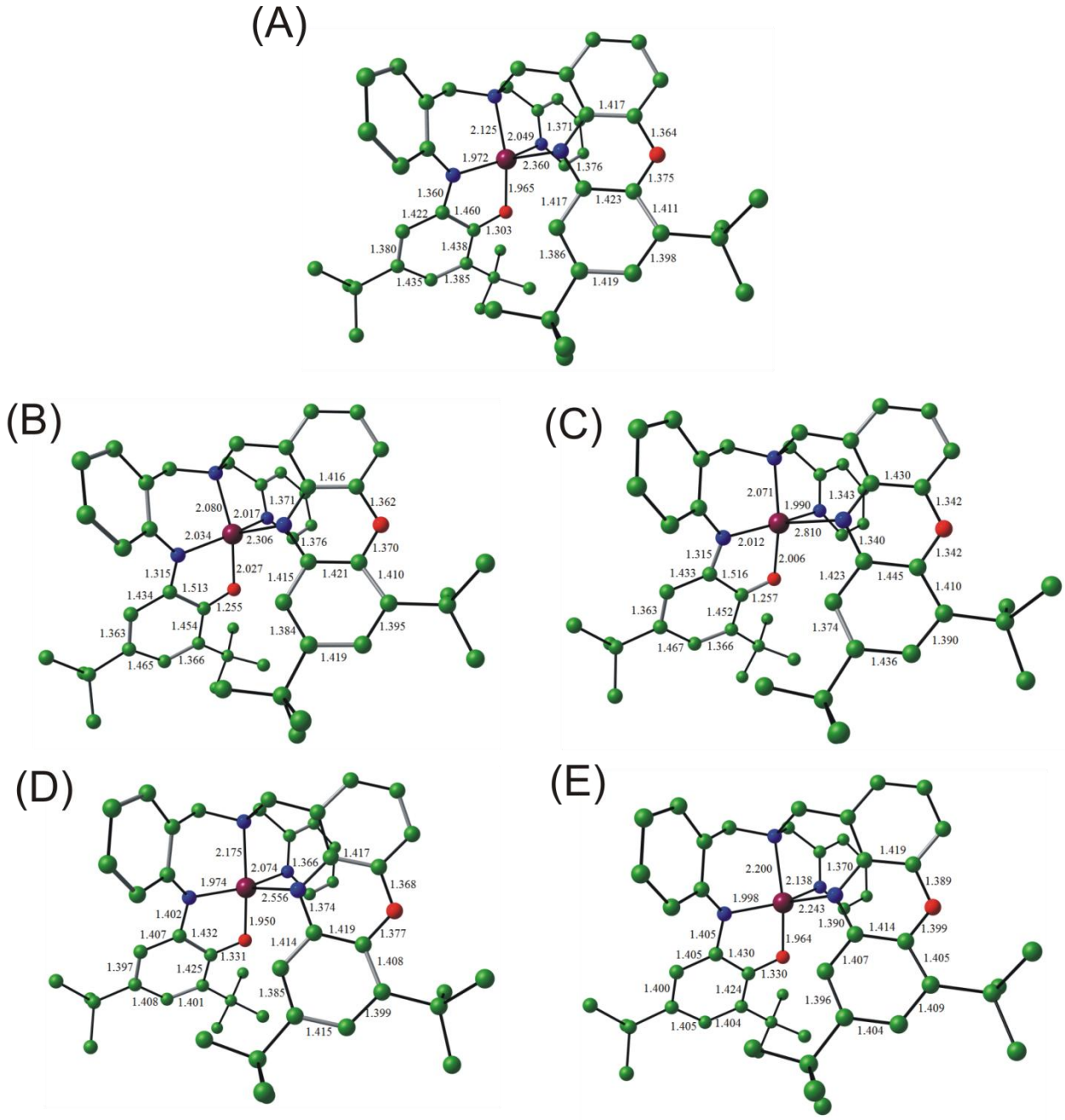



**Figure S13**. Optimized geometry and bond distances of (A) complex **1** (BS-doublet); (B) complex $\mathbf{1}^{+}$ (triplet); (C) $\mathbf{1}^{2+}$ (doublet); (D) $\mathbf{1}^{1-}$ (triplet); (E) $\mathbf{1}^{2-}$ (doublet). (H atoms were omitted for clarity)

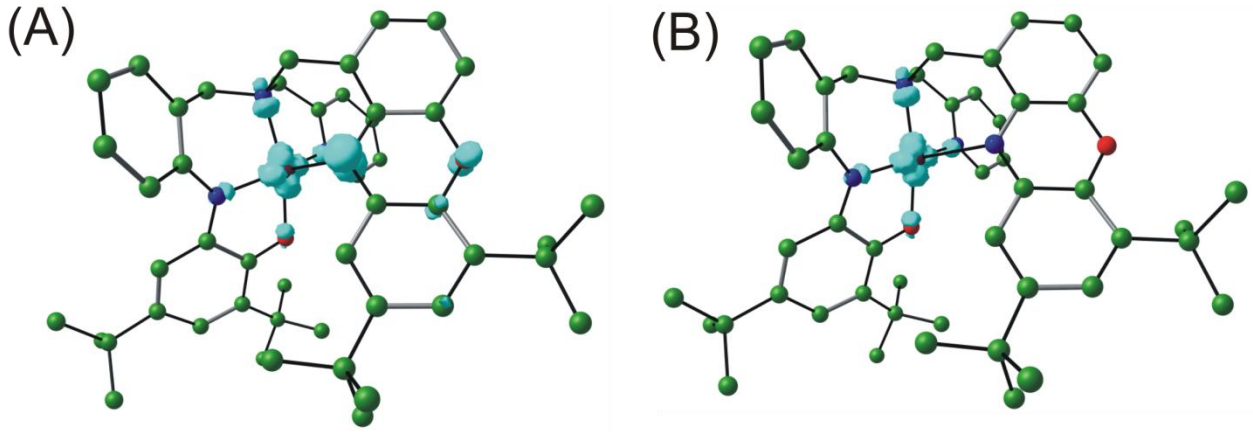



**Figure S14**. Spin Density of (A) complex $\mathbf{1}^{+}$ (triplet) and (B) $\mathbf{1}^{2+}$ (doublet). (isovalue 0.02) (H atoms were omitted for clarity)

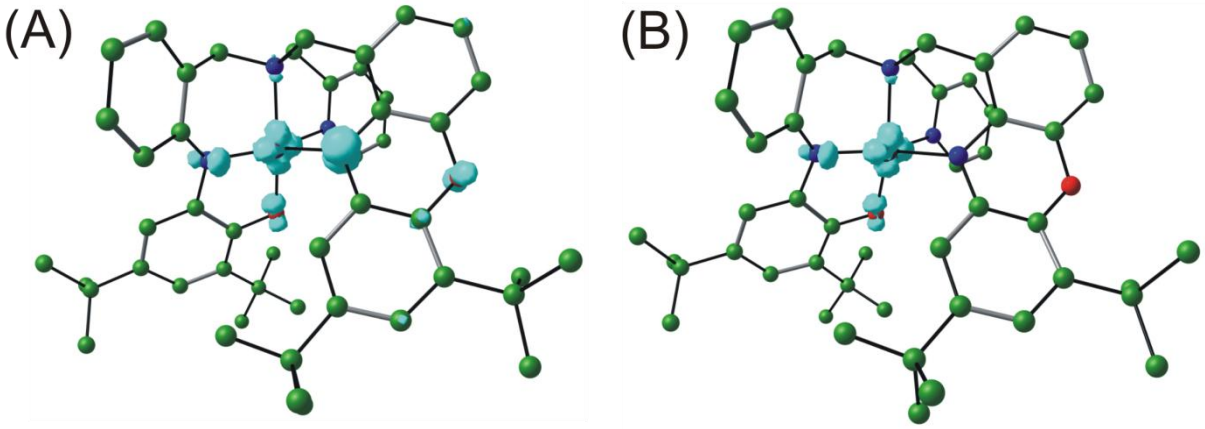



**Figure S15**. Spin Density of (A) $\mathbf{1}^{1-}$ (triplet) and (B) $\mathbf{1}^{2-}$ (doublet). (isovalue 0.02) (H atoms were omitted for clarity)

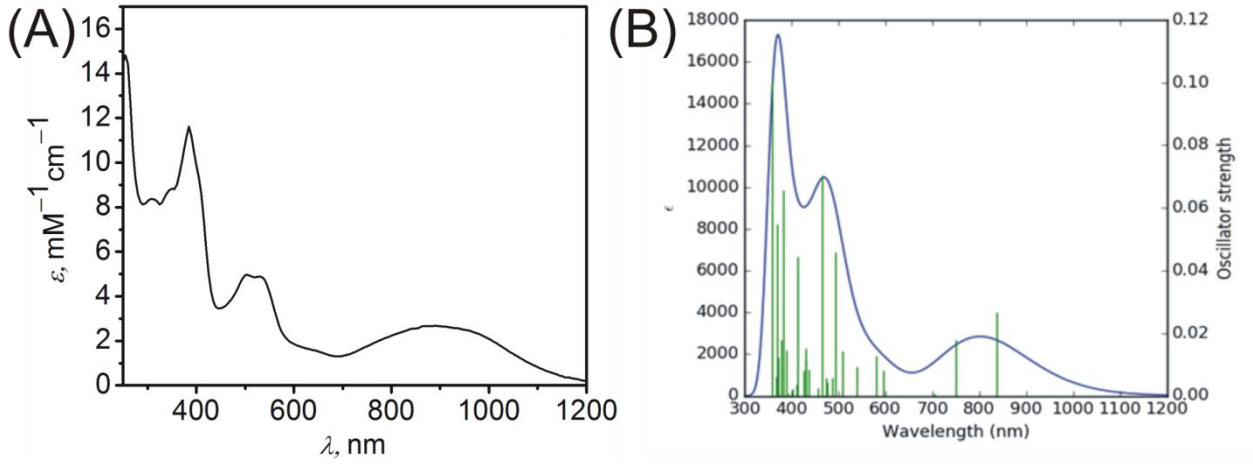



**Figure S16**. (A) Experimental and (B) theoretical UV-Vis/NIR plots of complex **1**.

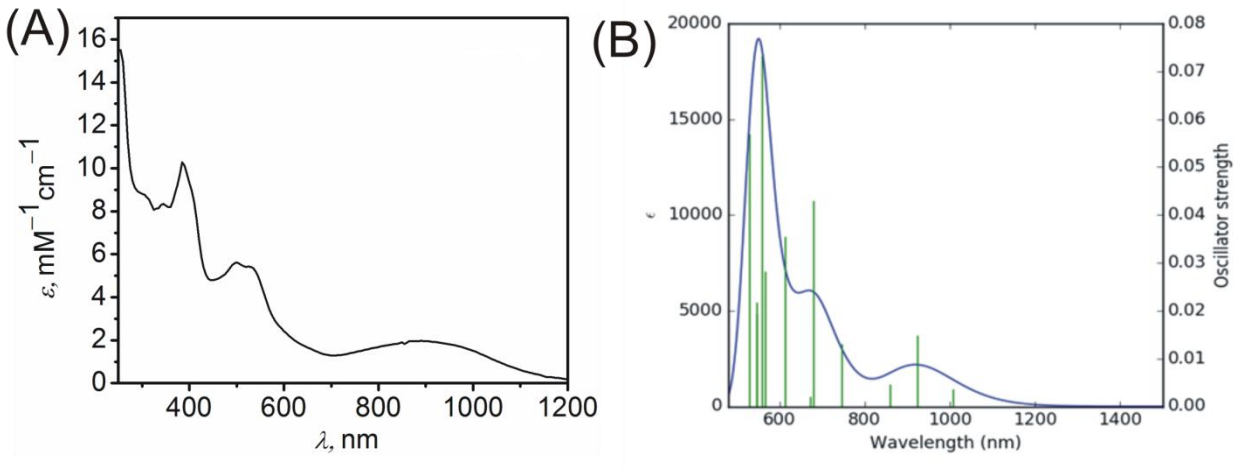



**Figure S17**. (A) Experimental and (B) theoretical UV-Vis/NIR plots of $\mathbf{1}^{1+}$.

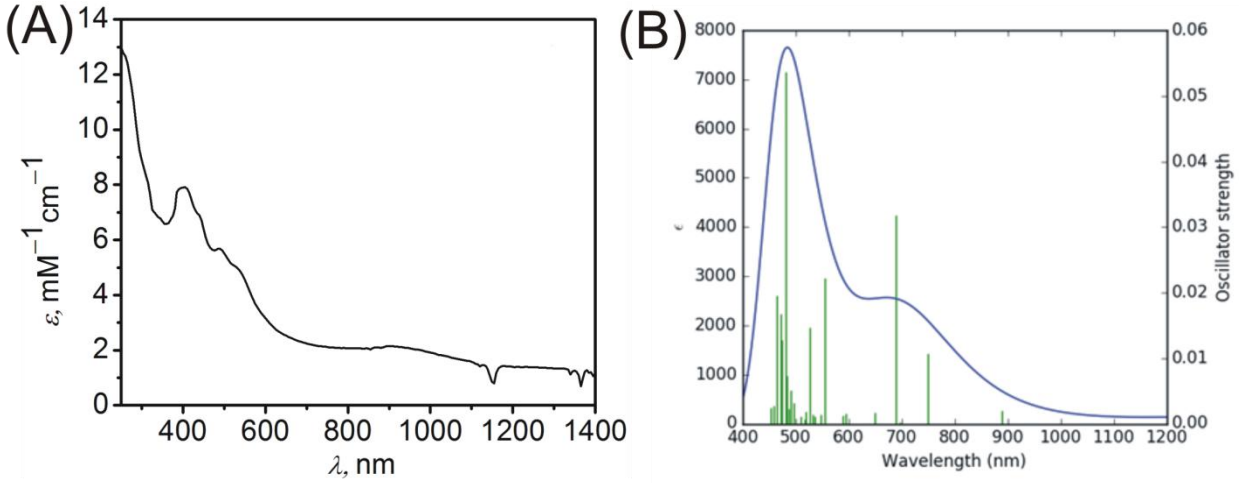



**Figure S18**. (A) Experimental and (B) theoretical UV-Vis/NIR plots of $\mathbf{1}^{2+}$.

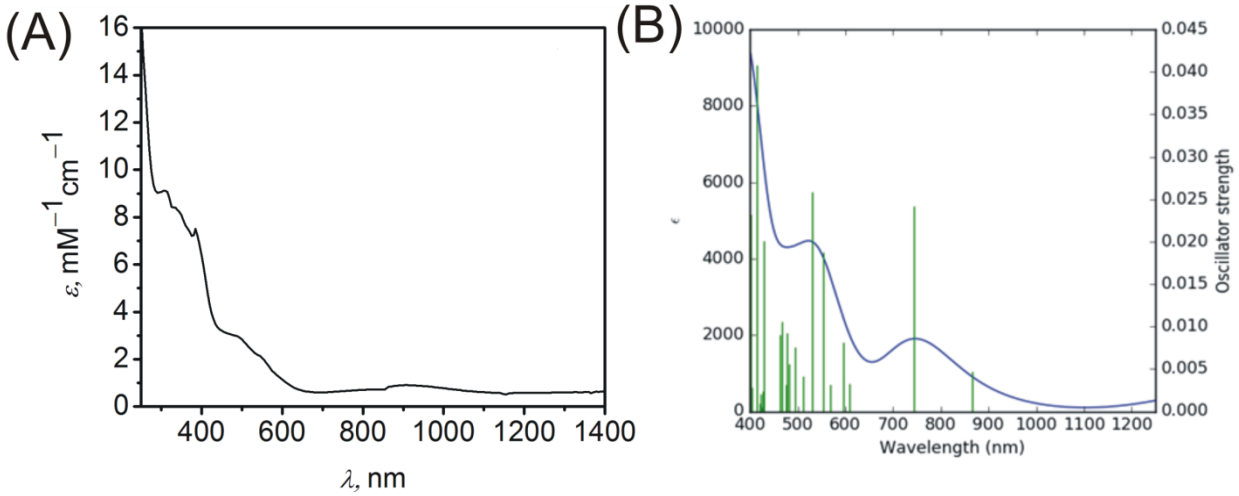



**Figure S19**. (A) Experimental and (B) theoretical UV-Vis/NIR plots of $\mathbf{1}^{1-}$.

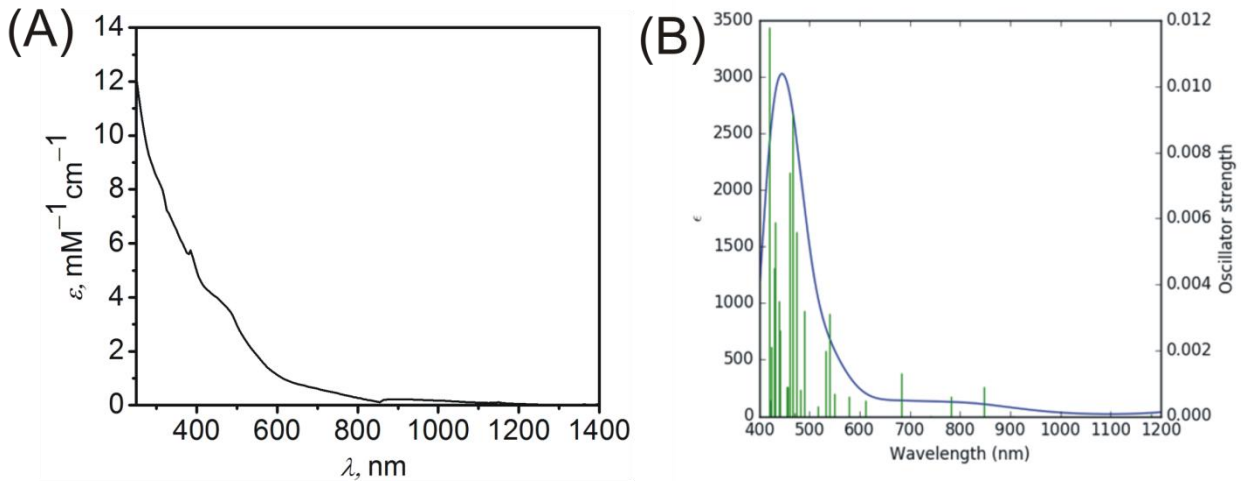



**Figure S20**. (A) Experimental and (B) theoretical UV-Vis/NIR plots of $\mathbf{1}^{2-}$.

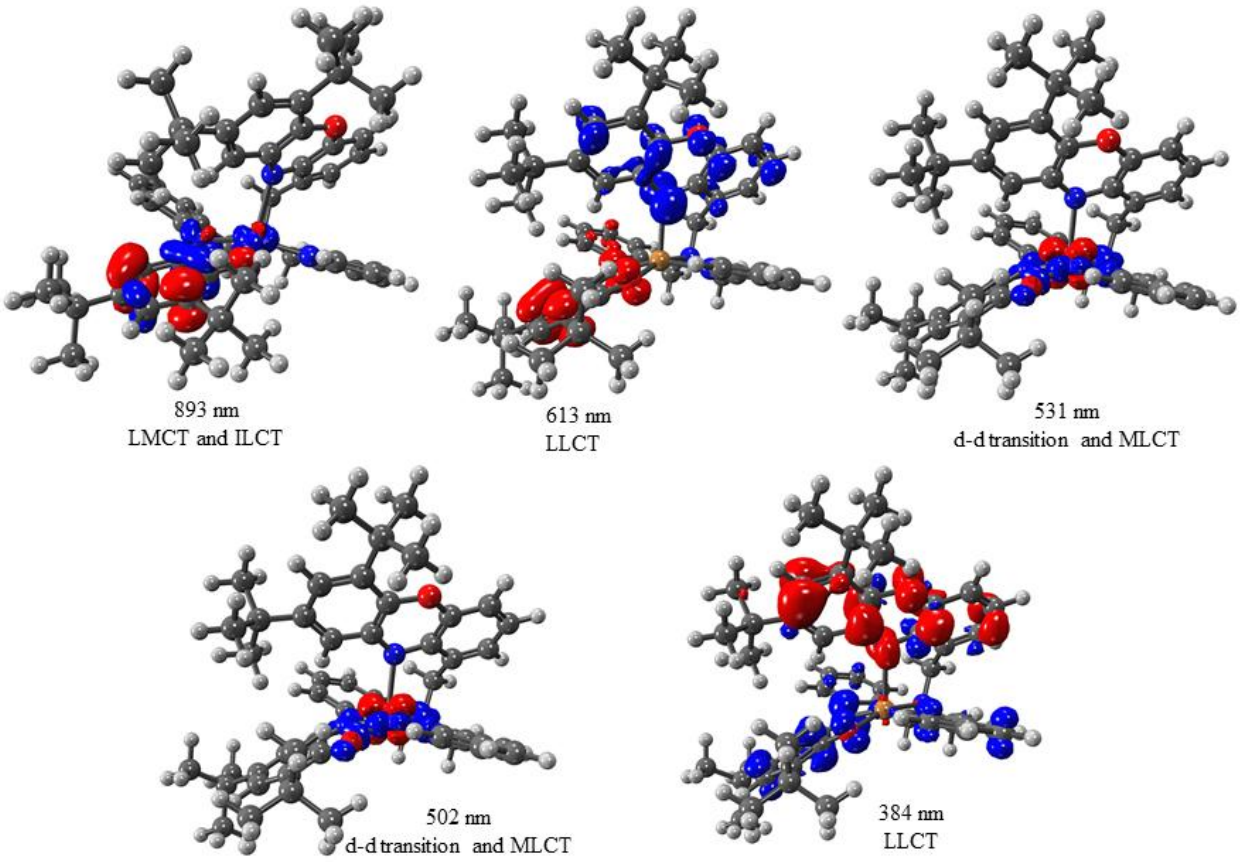



**Figure S21**. Electron density differences between the ground and excited states for the complex **1**. Red corresponds to negative values (higher electron density in the ground state) while blue corresponds to positive ones (higher electron density in the excited state). (LLCT: ligand-to-ligand charge transfer; MLCT: metal-to-ligand charge transfer)

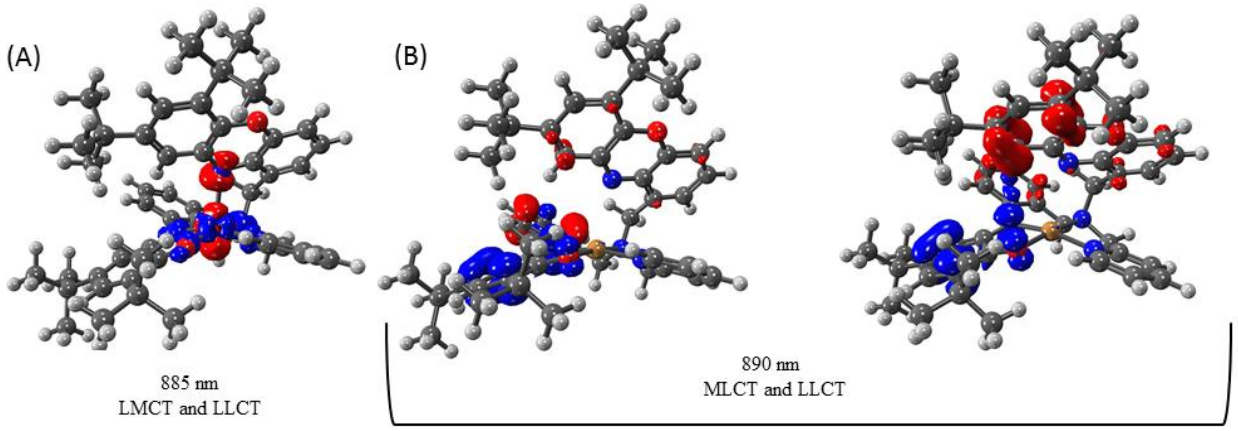



**Figure S22**. Electron density differences between the ground and excited states for (A) $\mathbf{1}^{1+}$ and (B) $\mathbf{1}^{2+}$. Red corresponds to negative values (higher electron density in the ground state) while blue corresponds to positive ones (higher electron density in the excited state). (LLCT: ligand-to-ligand charge transfer)

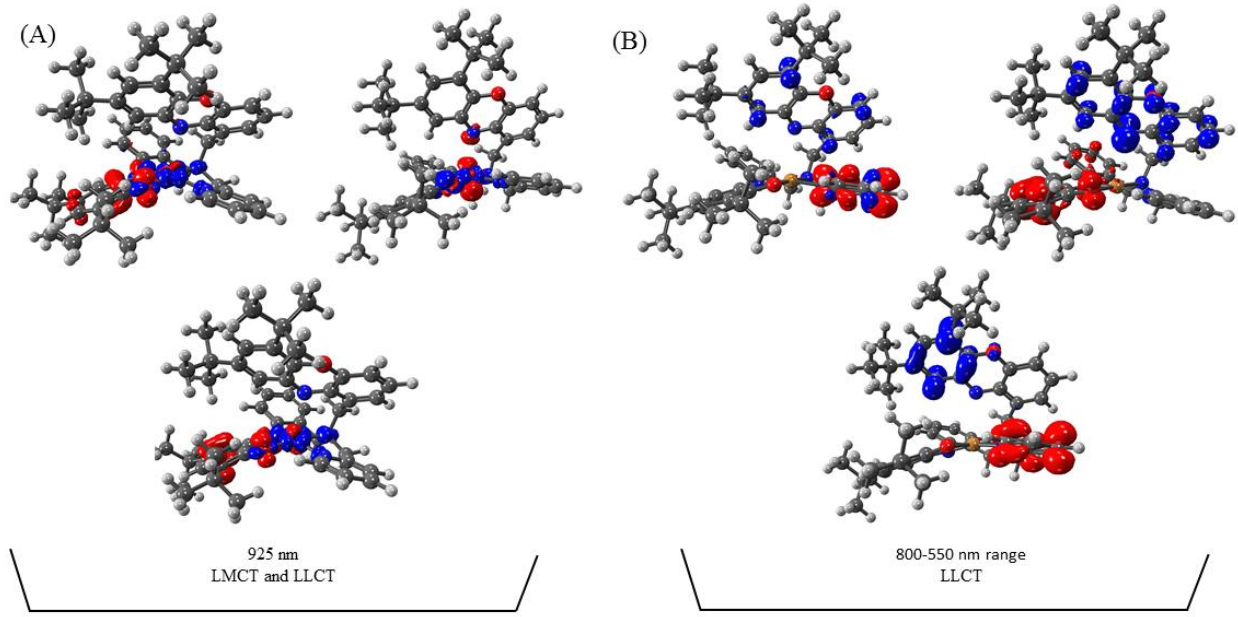



**Figure S23**. Electron density differences between the ground and excited states for (A) $\mathbf{1}^{1-}$ and (B) $\mathbf{1}^{2-}$. Red corresponds to negative values (higher electron density in the ground state) while blue corresponds to positive ones (higher electron density in the excited state). (LMCT: ligand-to-metal charge transfer)

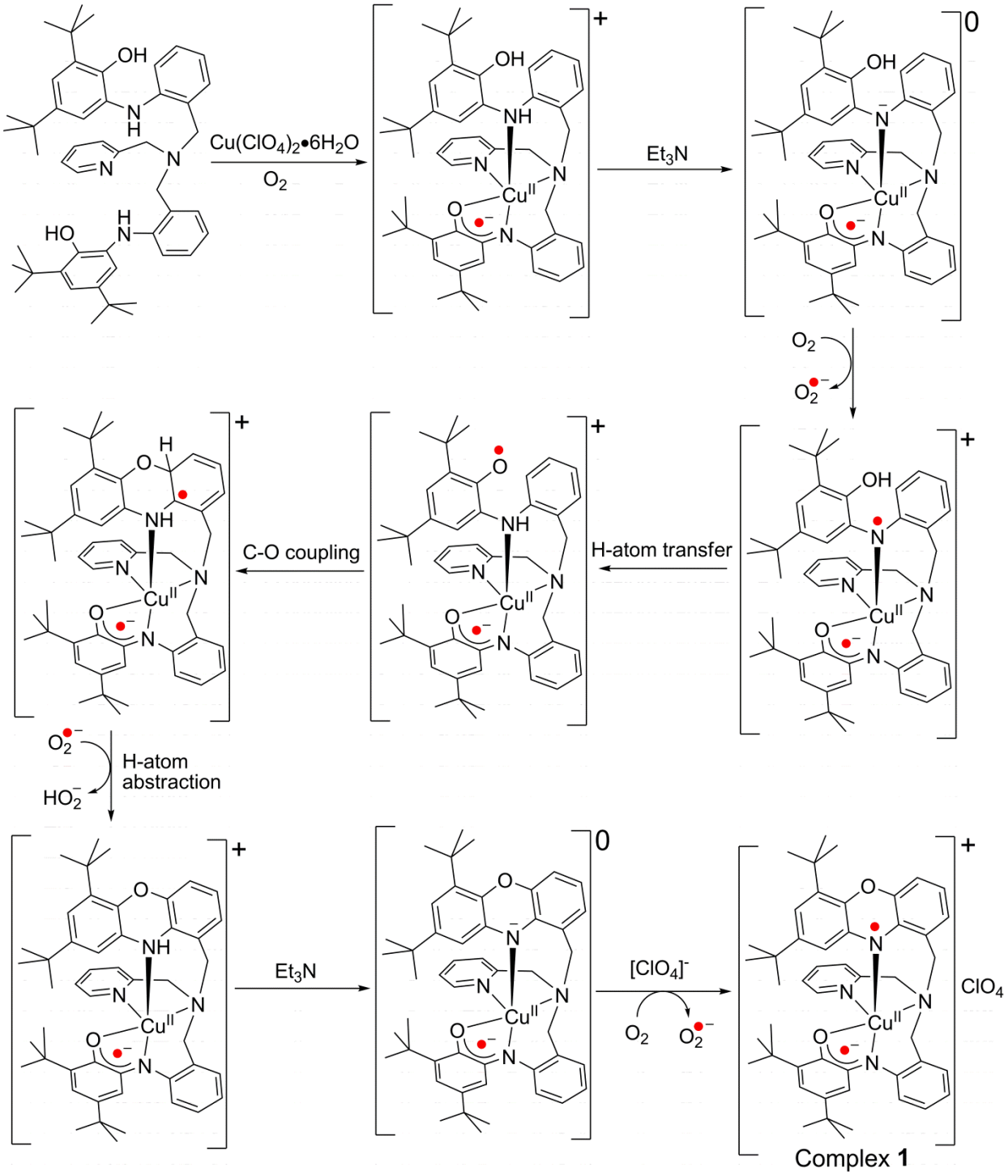



**Figure S24**. Plausible mechanism for the formation of complex **1**.

Optimized coordinates of complex **1**:

| | | | |
|---|---|---|---|
| Cu | -0.007658782 | -1.482474188 | 0.416847207 |
| O | -0.930544963 | -0.145124215 | 1.521209962 |
| O | 4.237093657 | 0.852284940 | -0.277516954 |
| N | 1.215059228 | -2.057799397 | 1.956561968 |
| N | 1.764752149 | -0.426934384 | -0.729722197 |
| N | -1.640715119 | -1.345516236 | -0.679152961 |
| N | 0.585476946 | -3.365969478 | -0.367755963 |
| C | 1.632819265 | -3.336257234 | 1.896474950 |
| C | -2.603654196 | -0.588362020 | -0.087528034 |
| C | -2.163711048 | 0.051373057 | 1.148398240 |
| C | -3.091810154 | 0.850595277 | 1.902298017 |
| C | 2.937381416 | -1.135684228 | -0.684376998 |
| C | 4.179447204 | -0.501276379 | -0.432511912 |
| C | -4.839488400 | 0.324718506 | 0.193890015 |
| C | 0.731743125 | 1.726695309 | -1.045001239 |
| C | 1.878324171 | 0.943517743 | -0.764583865 |
| C | 2.941845026 | -2.546792513 | -0.899733088 |
| C | 1.012975961 | -4.177033627 | 0.801347925 |
| C | -1.729825393 | -1.904988883 | -1.959176104 |
| C | -6.309523218 | 0.505251558 | -0.219934002 |
| C | -2.676130312 | 1.504427106 | 3.235400284 |
| C | -3.947868127 | -0.442585859 | -0.528386129 |
| C | 4.142829197 | -3.246329382 | -0.808214000 |
| C | 1.687182173 | -3.237705380 | -1.372826016 |
| C | 2.512045148 | -3.860685647 | 2.846177188 |
| C | 3.120303174 | 1.605108899 | -0.553108232 |
| C | 5.373749454 | -1.215175117 | -0.323377042 |
| C | 1.635066152 | -1.262041171 | 2.956476248 |
| C | 2.076093584 | 3.710859163 | -0.896047369 |
| C | 0.814640328 | 3.106748299 | -1.138142256 |
| C | -1.182356074 | -3.198755289 | -2.169773303 |
| C | -0.619392974 | -3.992922278 | -1.015867915 |
| C | 3.247289309 | 3.009320946 | -0.594180324 |
| C | -1.493820806 | 2.475218115 | 3.008724034 |
| C | -1.220332479 | -3.756727188 | -3.452984210 |
| C | -2.270780010 | 0.401161335 | 4.242910373 |
| C | -2.259523352 | -1.202598162 | -3.061909523 |
| C | 2.506235311 | -1.715309002 | 3.942837239 |
| C | 5.351153586 | -2.594518480 | -0.505188057 |
| C | -6.594212111 | 2.009622571 | -0.445286251 |
| C | -0.382715803 | 3.997969571 | -1.514986309 |
| C | -6.646638230 | -0.249107544 | -1.518152376 |
| C | -1.673004985 | 3.181432142 | -1.707009915 |
| C | -3.827195077 | 2.311234553 | 3.865759398 |
| C | -7.229113682 | -0.029963603 | 0.903955923 |

| | | | |
|---|---|---|---|
| C | 2.954129876 | -3.037752581 | 3.882407314 |
| C | -1.770833454 | -3.062854104 | -4.533514410 |
| C | -2.281629202 | -1.777532838 | -4.331622177 |
| C | 4.589125647 | 3.732908920 | -0.336839311 |
| C | -0.067327751 | 4.728960206 | -2.841916253 |
| C | 5.636904538 | 3.303431840 | -1.392274338 |
| C | 5.097636408 | 3.410780208 | 1.089437311 |
| C | -0.626894591 | 5.040612267 | -0.399762190 |
| C | 4.436008739 | 5.263779014 | -0.435404924 |
| C | -4.374797219 | 0.962523144 | 1.392293918 |
| H | -0.198273719 | 1.189450224 | -1.216931986 |
| H | 1.696284022 | -4.988305213 | 0.496350797 |
| H | 0.113937683 | -4.658661125 | 1.220301257 |
| H | -4.264133556 | -0.972914598 | -1.422508880 |
| H | 4.150491154 | -4.321564634 | -1.001266327 |
| H | 1.946344085 | -4.249876463 | -1.732943305 |
| H | 1.265802034 | -2.681370225 | -2.220882300 |
| H | 2.841029881 | -4.898605436 | 2.773585182 |
| H | 6.298264443 | -0.675783160 | -0.113370934 |
| H | 1.242235125 | -0.244206304 | 2.948426403 |
| H | 2.136104401 | 4.794299308 | -0.957937294 |
| H | -0.353638043 | -5.007187316 | -1.363724167 |
| H | -1.374968125 | -4.096656365 | -0.222097808 |
| H | -0.630702021 | 1.968586992 | 2.557396167 |
| H | -1.178579865 | 2.915225294 | 3.969200321 |
| H | -1.794210918 | 3.303083112 | 2.346061295 |
| H | -0.815012340 | -4.760097524 | -3.607294413 |
| H | -3.117061434 | -0.276572902 | 4.441045448 |
| H | -1.973944912 | 0.856690340 | 5.202048371 |
| H | -1.430079819 | -0.198229797 | 3.869033418 |
| H | -2.633354269 | -0.188795096 | -2.916579458 |
| H | 2.824372439 | -1.042808329 | 4.740022127 |
| H | 6.277490531 | -3.166847488 | -0.437513166 |
| H | -6.415148055 | 2.607891319 | 0.461281162 |
| H | -7.647560592 | 2.156007815 | -0.734154056 |
| H | -5.961135142 | 2.416498491 | -1.250196068 |
| H | -6.041694441 | 0.102990593 | -2.368744478 |
| H | -7.703892569 | -0.085646809 | -1.777017949 |
| H | -6.498248463 | -1.335572996 | -1.414501370 |
| H | -1.576476176 | 2.449815491 | -2.525231186 |
| H | -2.501860073 | 3.857414273 | -1.967692154 |
| H | -1.960971073 | 2.641579271 | -0.791548092 |
| H | -4.167470336 | 3.130566567 | 3.212716043 |
| H | -3.479389096 | 2.764772264 | 4.806582571 |
| H | -4.695704062 | 1.679139208 | 4.109102085 |
| H | -7.051667321 | -1.102390512 | 1.083603132 |
| H | -8.286200801 | 0.097577639 | 0.619850183 |

| | | | |
|---|---|---|---|
| H | -7.076815412 | 0.502165396 | 1.855429317 |
| H | 3.641325272 | -3.425286544 | 4.637145307 |
| H | -1.790423067 | -3.518307966 | -5.524860251 |
| H | -2.692921106 | -1.212276814 | -5.170491415 |
| H | 0.824363431 | 5.369509157 | -2.759846153 |
| H | -0.913269972 | 5.374060611 | -3.129260028 |
| H | 0.107354189 | 4.010922243 | -3.659147433 |
| H | 5.857774655 | 2.228944845 | -1.349720020 |
| H | 6.579638040 | 3.848463769 | -1.223521301 |
| H | 5.288508525 | 3.542645886 | -2.409789053 |
| H | 4.369584823 | 3.741410153 | 1.847925054 |
| H | 6.042833760 | 3.945204778 | 1.277332277 |
| H | 5.283250620 | 2.338412038 | 1.234455161 |
| H | -0.844653674 | 4.549099209 | 0.561223165 |
| H | -1.486210708 | 5.678998471 | -0.660701079 |
| H | 0.240245413 | 5.702274332 | -0.251771952 |
| H | 4.115939584 | 5.588123391 | -1.437912172 |
| H | 5.409972695 | 5.735223025 | -0.235509805 |
| H | 3.722440736 | 5.659979312 | 0.303984812 |
| H | -5.096307114 | 1.557180257 | 1.947917329 |

Optimized coordinates of complex $\mathbf{1}^{1+}$:

| | | | |
|---|---|---|---|
| Cu | 0.078237269 | -1.521888368 | 0.394560378 |
| O | -0.904643853 | -0.161488492 | 1.530604975 |
| O | 4.154116019 | 0.895180577 | -0.289597012 |
| N | 1.306802687 | -2.063398622 | 1.899302344 |
| N | 1.713876519 | -0.405067721 | -0.787021509 |
| N | -1.652036337 | -1.360190322 | -0.661862623 |
| N | 0.594085072 | -3.382881454 | -0.377240406 |
| C | 1.708203739 | -3.348244157 | 1.850791607 |
| C | -2.580575189 | -0.639955214 | -0.071634724 |
| C | -2.104854367 | 0.014048598 | 1.207041134 |
| C | -3.030735691 | 0.825312775 | 1.981486217 |
| C | 2.891991767 | -1.103278471 | -0.733831258 |
| C | 4.121264695 | -0.455733268 | -0.461376943 |
| C | -4.788546093 | 0.295256563 | 0.249557874 |
| C | 0.666797730 | 1.742410286 | -1.123910563 |
| C | 1.809094028 | 0.966893090 | -0.812897219 |
| C | 2.915589897 | -2.512082190 | -0.953016475 |
| C | 1.064462262 | -4.198135628 | 0.783333673 |
| C | -1.769573483 | -1.942319692 | -1.933302512 |
| C | -6.260168443 | 0.499742294 | -0.110919256 |
| C | -2.589103939 | 1.478383118 | 3.301431021 |
| C | -3.939850563 | -0.468160466 | -0.494883388 |
| C | 4.122595576 | -3.194310729 | -0.858596966 |
| C | 1.669212372 | -3.220354716 | -1.416486843 |

| | | | |
|---|---|---|---|
| C | 2.605662953 | -3.859301319 | 2.786492873 |
| C | 3.038244187 | 1.637931647 | -0.570605477 |
| C | 5.323168047 | -1.151547374 | -0.346831765 |
| C | 1.765243755 | -1.244299446 | 2.863217754 |
| C | 1.986607594 | 3.736002491 | -0.915683549 |
| C | 0.740969330 | 3.122215091 | -1.205917161 |
| C | -1.221304048 | -3.235732078 | -2.129238326 |
| C | -0.622218251 | -4.023542591 | -0.987261122 |
| C | 3.152658658 | 3.042713618 | -0.590530059 |
| C | -1.426333244 | 2.467146575 | 3.039754988 |
| C | -1.314498512 | -3.810004754 | -3.397307355 |
| C | -2.140660617 | 0.379267155 | 4.298040059 |
| C | -2.326739446 | -1.239357988 | -3.019045637 |
| C | 2.655929500 | -1.688389226 | 3.831840724 |
| C | 5.318464190 | -2.526742517 | -0.541834110 |
| C | -6.512298648 | 2.015108023 | -0.325224400 |
| C | -0.442084199 | 4.009236813 | -1.632426616 |
| C | -6.653859383 | -0.250123564 | -1.396135215 |
| C | -1.722912221 | 3.194803393 | -1.892589731 |
| C | -3.744320628 | 2.264484918 | 3.950649483 |
| C | -7.148207244 | -0.016453708 | 1.050679840 |
| C | 3.082710951 | -3.017458105 | 3.789289581 |
| C | -1.891740401 | -3.119957092 | -4.467189979 |
| C | -2.382435352 | -1.826943706 | -4.278598087 |
| C | 4.481885232 | 3.770537127 | -0.291429553 |
| C | -0.066965793 | 4.746424113 | -2.941967266 |
| C | 5.557542767 | 3.365381562 | -1.330081724 |
| C | 4.963222741 | 3.427372031 | 1.140463227 |
| C | -0.743801487 | 5.048345135 | -0.526812885 |
| C | 4.319425170 | 5.302703704 | -0.368251802 |
| C | -4.290736355 | 0.940243724 | 1.466696239 |
| H | -0.246271683 | 1.206284940 | -1.346575120 |
| H | 1.741149786 | -4.989833477 | 0.445343402 |
| H | 0.190767869 | -4.691085403 | 1.222307898 |
| H | -4.278506540 | -0.992447059 | -1.376032301 |
| H | 4.147376417 | -4.262262915 | -1.051597434 |
| H | 1.930975190 | -4.218095665 | -1.788373563 |
| H | 1.219106375 | -2.664000511 | -2.241220698 |
| H | 2.920948346 | -4.895070532 | 2.727263122 |
| H | 6.233147595 | -0.606235511 | -0.122383881 |
| H | 1.398614411 | -0.224437301 | 2.843379957 |
| H | 2.036239128 | 4.814746717 | -0.964700708 |
| H | -0.350794773 | -5.024373934 | -1.342984652 |
| H | -1.351607067 | -4.146950959 | -0.182033799 |
| H | -0.559236633 | 1.973850718 | 2.597499336 |
| H | -1.115060603 | 2.920867381 | 3.986028686 |
| H | -1.747063341 | 3.272684525 | 2.371472916 |

| | | | |
|---|---|---|---|
| H | -0.925388131 | -4.811512386 | -3.552712425 |
| H | -2.957794428 | -0.321084117 | 4.500051357 |
| H | -1.855338298 | 0.844275842 | 5.247027908 |
| H | -1.283240541 | -0.184671218 | 3.926640711 |
| H | -2.667992625 | -0.219990624 | -2.879694216 |
| H | 3.005873886 | -1.005945842 | 4.597289794 |
| H | 6.245187964 | -3.085240948 | -0.469299785 |
| H | -6.289338281 | 2.608406737 | 0.566243999 |
| H | -7.567065324 | 2.173968620 | -0.569747152 |
| H | -5.908406334 | 2.400929038 | -1.152283989 |
| H | -6.072757145 | 0.086192919 | -2.260834124 |
| H | -7.708347712 | -0.061592528 | -1.615436851 |
| H | -6.528731189 | -1.332759360 | -1.291491473 |
| H | -1.579399880 | 2.449219108 | -2.681434785 |
| H | -2.521404176 | 3.868184088 | -2.218687802 |
| H | -2.073891148 | 2.686011110 | -0.989249241 |
| H | -4.099997591 | 3.078559027 | 3.310505882 |
| H | -3.389122571 | 2.712519715 | 4.882735410 |
| H | -4.593636883 | 1.619660744 | 4.199352207 |
| H | -6.986748386 | -1.085015506 | 1.223435045 |
| H | -8.201143496 | 0.131865150 | 0.791852369 |
| H | -6.963853532 | 0.513161170 | 1.989597446 |
| H | 3.782175322 | -3.393488812 | 4.528480876 |
| H | -1.938910203 | -3.585393883 | -5.445890601 |
| H | -2.800021290 | -1.271119207 | -5.111241555 |
| H | 0.815375356 | 5.380700727 | -2.817133824 |
| H | -0.895563172 | 5.387576327 | -3.260601292 |
| H | 0.141228412 | 4.033702265 | -3.746659591 |
| H | 5.788667281 | 2.299756169 | -1.293619294 |
| H | 6.482467339 | 3.918022001 | -1.133935297 |
| H | 5.228444790 | 3.611498726 | -2.344982832 |
| H | 4.219818666 | 3.735173799 | 1.883552442 |
| H | 5.892665427 | 3.965669650 | 1.354203739 |
| H | 5.156168703 | 2.361022723 | 1.267683259 |
| H | -1.011359325 | 4.555266770 | 0.413272615 |
| H | -1.584012189 | 5.682150780 | -0.829159894 |
| H | 0.109383583 | 5.704119573 | -0.331409423 |
| H | 4.024277618 | 5.638311091 | -1.367679767 |
| H | 5.279945908 | 5.771929934 | -0.136072109 |
| H | 3.587671462 | 5.676990773 | 0.354978978 |
| H | -5.007949331 | 1.538118763 | 2.012707145 |

Optimized coordinates of complex $\mathbf{1}^{2+}$:

| | | | |
|---|---|---|---|
| Cu | -0.201100000 | -1.640900000 | 0.534400000 |
| O | -1.121100000 | -0.210900000 | 1.599300000 |
| O | 4.344900000 | 0.691400000 | -0.402500000 |

| | | | |
|---|---|---|---|
| N | 1.083100000 | -2.157800000 | 1.963600000 |
| N | 1.857900000 | -0.389000000 | -0.910200000 |
| N | -1.783100000 | -1.320900000 | -0.667500000 |
| N | 0.428600000 | -3.395000000 | -0.369300000 |
| C | 1.508100000 | -3.435400000 | 1.872900000 |
| C | -2.707500000 | -0.556600000 | -0.128000000 |
| C | -2.280200000 | 0.055200000 | 1.192000000 |
| C | -3.195400000 | 0.929000000 | 1.904000000 |
| C | 2.928100000 | -1.189900000 | -0.780500000 |
| C | 4.218700000 | -0.640400000 | -0.503000000 |
| C | -4.874200000 | 0.497800000 | 0.064000000 |
| C | 0.906200000 | 1.797600000 | -1.103200000 |
| C | 2.017000000 | 0.940800000 | -0.864100000 |
| C | 2.804100000 | -2.611800000 | -0.935600000 |
| C | 0.889500000 | -4.255500000 | 0.766600000 |
| C | -1.843000000 | -1.867000000 | -1.958400000 |
| C | -6.313700000 | 0.767900000 | -0.368800000 |
| C | -2.796100000 | 1.567700000 | 3.243900000 |
| C | -4.024700000 | -0.307600000 | -0.633800000 |
| C | 3.940800000 | -3.378100000 | -0.793300000 |
| C | 1.504800000 | -3.217600000 | -1.406000000 |
| C | 2.399200000 | -3.965000000 | 2.802600000 |
| C | 3.312700000 | 1.525300000 | -0.603200000 |
| C | 5.354900000 | -1.434900000 | -0.332000000 |
| C | 1.502500000 | -1.370000000 | 2.973100000 |
| C | 2.385100000 | 3.674800000 | -0.805300000 |
| C | 1.076900000 | 3.160800000 | -1.099400000 |
| C | -1.332700000 | -3.175500000 | -2.161600000 |
| C | -0.789400000 | -4.006200000 | -1.021800000 |
| C | 3.522200000 | 2.918000000 | -0.545100000 |
| C | -1.559600000 | 2.477200000 | 3.039100000 |
| C | -1.385200000 | -3.714500000 | -3.447000000 |
| C | -2.480300000 | 0.458000000 | 4.278200000 |
| C | -2.307600000 | -1.112100000 | -3.053400000 |
| C | 2.383200000 | -1.838000000 | 3.938800000 |
| C | 5.200500000 | -2.799700000 | -0.477100000 |
| C | -6.503200000 | 2.296300000 | -0.556000000 |
| C | -0.047900000 | 4.151400000 | -1.422800000 |
| C | -6.666200000 | 0.064000000 | -1.691200000 |
| C | -1.387400000 | 3.434300000 | -1.667800000 |
| C | -3.936400000 | 2.434300000 | 3.811500000 |
| C | -7.275400000 | 0.256100000 | 0.735900000 |
| C | 2.839300000 | -3.154900000 | 3.848400000 |
| C | -1.880200000 | -2.975000000 | -4.525700000 |
| C | -2.322300000 | -1.665900000 | -4.329000000 |
| C | 4.896600000 | 3.550300000 | -0.242000000 |
| C | 0.335600000 | 4.932100000 | -2.705200000 |

| | | | |
|---|---|---|---|
| C | 5.910800000 | 3.151400000 | -1.343000000 |
| C | 5.395100000 | 3.084700000 | 1.148800000 |
| C | -0.224900000 | 5.139300000 | -0.243600000 |
| C | 4.807400000 | 5.089000000 | -0.217700000 |
| C | -4.410800000 | 1.118700000 | 1.309500000 |
| H | -0.043900000 | 1.330400000 | -1.325700000 |
| H | 1.576100000 | -5.029500000 | 0.411300000 |
| H | 0.012800000 | -4.770400000 | 1.172700000 |
| H | -4.339900000 | -0.813700000 | -1.534100000 |
| H | 3.890600000 | -4.451000000 | -0.947900000 |
| H | 1.716500000 | -4.203100000 | -1.835300000 |
| H | 1.084300000 | -2.596600000 | -2.197400000 |
| H | 2.733600000 | -4.992300000 | 2.711100000 |
| H | 6.312000000 | -0.976600000 | -0.114100000 |
| H | 1.111700000 | -0.359300000 | 2.991800000 |
| H | 2.494500000 | 4.750900000 | -0.795000000 |
| H | -0.525400000 | -5.002400000 | -1.393100000 |
| H | -1.537700000 | -4.137900000 | -0.235500000 |
| H | -0.695500000 | 1.918000000 | 2.674700000 |
| H | -1.286800000 | 2.941200000 | 3.991900000 |
| H | -1.783500000 | 3.278300000 | 2.327000000 |
| H | -1.026700000 | -4.725800000 | -3.610700000 |
| H | -3.354600000 | -0.180100000 | 4.443300000 |
| H | -2.217100000 | 0.920100000 | 5.234700000 |
| H | -1.645000000 | -0.171200000 | 3.965800000 |
| H | -2.615100000 | -0.083300000 | -2.906200000 |
| H | 2.701300000 | -1.183600000 | 4.741600000 |
| H | 6.062700000 | -3.448200000 | -0.368600000 |
| H | -6.324800000 | 2.860300000 | 0.363900000 |
| H | -7.534500000 | 2.492800000 | -0.864300000 |
| H | -5.835500000 | 2.684300000 | -1.331200000 |
| H | -6.029000000 | 0.399600000 | -2.515700000 |
| H | -7.700200000 | 0.297500000 | -1.958800000 |
| H | -6.587500000 | -1.024800000 | -1.609200000 |
| H | -1.332400000 | 2.743700000 | -2.516000000 |
| H | -2.157500000 | 4.175200000 | -1.898700000 |
| H | -1.717600000 | 2.879400000 | -0.783500000 |
| H | -4.200500000 | 3.259300000 | 3.141900000 |
| H | -3.610200000 | 2.872700000 | 4.758500000 |
| H | -4.837500000 | 1.846800000 | 4.015600000 |
| H | -7.169100000 | -0.823400000 | 0.879500000 |
| H | -8.307200000 | 0.460800000 | 0.434700000 |
| H | -7.110700000 | 0.747200000 | 1.699100000 |
| H | 3.530700000 | -3.547800000 | 4.586200000 |
| H | -1.898200000 | -3.415100000 | -5.516900000 |
| H | -2.671000000 | -1.072100000 | -5.167000000 |
| H | 1.269700000 | 5.489100000 | -2.588200000 |

| | | | |
|---|---|---|---|
| H | -0.452000000 | 5.653900000 | -2.942300000 |
| H | 0.447200000 | 4.255400000 | -3.558100000 |
| H | 6.079700000 | 2.073900000 | -1.387900000 |
| H | 6.872500000 | 3.630700000 | -1.136500000 |
| H | 5.571000000 | 3.488500000 | -2.327200000 |
| H | 4.684400000 | 3.365600000 | 1.932400000 |
| H | 6.348700000 | 3.573000000 | 1.370500000 |
| H | 5.557100000 | 2.006600000 | 1.199300000 |
| H | -0.490200000 | 4.611000000 | 0.677400000 |
| H | -1.029700000 | 5.843000000 | -0.476200000 |
| H | 0.676500000 | 5.727500000 | -0.050000000 |
| H | 4.503500000 | 5.501700000 | -1.184900000 |
| H | 5.796800000 | 5.493200000 | 0.011500000 |
| H | 4.119000000 | 5.452300000 | 0.552400000 |
| H | -5.122200000 | 1.761100000 | 1.810600000 |

Optimized coordinates of complex $\mathbf{1}^{1-}$:

| | | | |
|---|---|---|---|
| Cu | 0.066700000 | -1.603700000 | 0.451100000 |
| O | -0.803200000 | -0.190900000 | 1.475700000 |
| O | 4.061200000 | 1.206300000 | -0.287700000 |
| N | 1.441200000 | -2.119000000 | 1.915600000 |
| N | 1.769100000 | -0.309000000 | -0.947900000 |
| N | -1.645700000 | -1.699000000 | -0.526900000 |
| N | 0.909700000 | -3.380500000 | -0.477700000 |
| C | 2.003900000 | -3.329700000 | 1.761400000 |
| C | -2.573800000 | -0.807500000 | 0.029600000 |
| C | -2.097100000 | -0.098800000 | 1.178900000 |
| C | -3.016600000 | 0.657400000 | 1.962600000 |
| C | 2.993100000 | -0.895600000 | -0.797000000 |
| C | 4.147900000 | -0.148800000 | -0.453600000 |
| C | -4.826700000 | 0.074100000 | 0.377200000 |
| C | 0.532500000 | 1.729500000 | -1.225700000 |
| C | 1.739200000 | 1.063800000 | -0.908400000 |
| C | 3.144800000 | -2.299400000 | -0.999900000 |
| C | 1.428400000 | -4.187000000 | 0.653200000 |
| C | -1.645200000 | -2.084400000 | -1.853400000 |
| C | -6.312800000 | 0.206600000 | -0.011700000 |
| C | -2.554000000 | 1.355900000 | 3.258500000 |
| C | -3.923700000 | -0.702100000 | -0.353300000 |
| C | 4.399000000 | -2.880000000 | -0.837400000 |
| C | 1.971200000 | -3.109000000 | -1.489700000 |
| C | 2.997200000 | -3.785400000 | 2.629700000 |
| C | 2.880800000 | 1.845200000 | -0.594100000 |
| C | 5.393600000 | -0.742500000 | -0.273200000 |
| C | 1.828600000 | -1.323200000 | 2.925700000 |
| C | 1.631300000 | 3.840000000 | -0.925100000 |

| | | | |
|---|---|---|---|
| C | 0.463300000 | 3.112900000 | -1.257700000 |
| C | -0.921700000 | -3.267100000 | -2.205600000 |
| C | -0.248800000 | -4.080000000 | -1.131300000 |
| C | 2.852900000 | 3.253000000 | -0.580200000 |
| C | -1.455500000 | 2.398800000 | 2.942400000 |
| C | -0.880900000 | -3.692500000 | -3.535700000 |
| C | -1.997000000 | 0.296700000 | 4.241500000 |
| C | -2.270900000 | -1.367900000 | -2.906100000 |
| C | 2.808100000 | -1.709100000 | 3.834500000 |
| C | 5.516100000 | -2.116800000 | -0.464200000 |
| C | -6.649700000 | 1.693000000 | -0.281800000 |
| C | -0.807900000 | 3.876500000 | -1.671900000 |
| C | -6.663100000 | -0.595100000 | -1.280200000 |
| C | -2.000200000 | 2.930300000 | -1.906600000 |
| C | -3.700900000 | 2.095900000 | 3.975300000 |
| C | -7.207300000 | -0.312400000 | 1.139800000 |
| C | 3.402300000 | -2.963600000 | 3.679600000 |
| C | -1.525000000 | -2.985400000 | -4.553100000 |
| C | -2.212400000 | -1.813000000 | -4.222800000 |
| C | 4.092100000 | 4.102000000 | -0.218900000 |
| C | -0.525200000 | 4.641300000 | -2.988100000 |
| C | 5.236300000 | 3.834200000 | -1.228200000 |
| C | 4.562400000 | 3.772500000 | 1.220000000 |
| C | -1.204700000 | 4.887800000 | -0.570700000 |
| C | 3.783000000 | 5.612700000 | -0.264500000 |
| C | -4.343700000 | 0.736600000 | 1.521500000 |
| H | -0.318200000 | 1.101500000 | -1.456400000 |
| H | 2.164100000 | -4.929600000 | 0.317700000 |
| H | 0.585100000 | -4.745700000 | 1.075500000 |
| H | -4.262900000 | -1.274300000 | -1.207000000 |
| H | 4.516000000 | -3.945500000 | -1.014200000 |
| H | 2.337100000 | -4.068000000 | -1.885700000 |
| H | 1.482000000 | -2.574800000 | -2.306400000 |
| H | 3.440500000 | -4.764500000 | 2.481600000 |
| H | 6.242300000 | -0.124700000 | 0.000900000 |
| H | 1.319600000 | -0.367300000 | 2.987800000 |
| H | 1.575000000 | 4.919800000 | -0.944500000 |
| H | 0.093100000 | -5.038900000 | -1.547300000 |
| H | -0.962500000 | -4.288700000 | -0.327900000 |
| H | -0.621200000 | 1.937700000 | 2.412100000 |
| H | -1.081000000 | 2.854100000 | 3.868200000 |
| H | -1.861300000 | 3.202200000 | 2.317000000 |
| H | -0.334200000 | -4.602100000 | -3.775900000 |
| H | -2.782800000 | -0.410500000 | 4.531400000 |
| H | -1.625600000 | 0.778600000 | 5.154700000 |
| H | -1.181000000 | -0.262400000 | 3.781200000 |
| H | -2.792400000 | -0.446600000 | -2.675600000 |

| | | | |
|---|---|---|---|
| H | 3.096200000 | -1.042800000 | 4.639800000 |
| H | 6.482100000 | -2.594500000 | -0.337700000 |
| H | -6.463100000 | 2.316700000 | 0.597600000 |
| H | -7.706000000 | 1.807300000 | -0.554300000 |
| H | -6.042700000 | 2.086200000 | -1.104600000 |
| H | -6.084000000 | -0.259300000 | -2.146800000 |
| H | -7.724100000 | -0.464400000 | -1.519600000 |
| H | -6.484300000 | -1.667200000 | -1.146800000 |
| H | -1.804900000 | 2.225900000 | -2.721800000 |
| H | -2.883500000 | 3.515500000 | -2.182000000 |
| H | -2.246000000 | 2.354300000 | -1.009200000 |
| H | -4.127600000 | 2.891000000 | 3.354300000 |
| H | -3.316600000 | 2.562400000 | 4.889200000 |
| H | -4.510800000 | 1.417900000 | 4.265100000 |
| H | -7.006300000 | -1.370200000 | 1.341900000 |
| H | -8.268300000 | -0.211800000 | 0.880800000 |
| H | -7.036700000 | 0.242500000 | 2.067200000 |
| H | 4.173500000 | -3.296400000 | 4.367200000 |
| H | -1.483400000 | -3.335900000 | -5.579700000 |
| H | -2.701300000 | -1.232300000 | -5.001300000 |
| H | 0.293300000 | 5.359200000 | -2.874800000 |
| H | -1.416000000 | 5.196600000 | -3.302500000 |
| H | -0.255800000 | 3.948400000 | -3.792300000 |
| H | 5.556300000 | 2.791200000 | -1.219200000 |
| H | 6.102700000 | 4.457400000 | -0.979900000 |
| H | 4.921200000 | 4.087800000 | -2.246100000 |
| H | 3.767700000 | 3.984200000 | 1.943500000 |
| H | 5.426500000 | 4.394600000 | 1.478800000 |
| H | 4.854500000 | 2.727000000 | 1.328200000 |
| H | -1.407100000 | 4.376400000 | 0.375400000 |
| H | -2.111600000 | 5.426800000 | -0.866100000 |
| H | -0.423800000 | 5.632700000 | -0.390500000 |
| H | 3.482300000 | 5.942900000 | -1.264100000 |
| H | 4.685400000 | 6.169200000 | 0.007400000 |
| H | 2.996900000 | 5.893600000 | 0.443800000 |
| H | -5.042200000 | 1.333700000 | 2.095500000 |

Optimized coordinates of complex $\mathbf{1}^{2-}$ in doublet state:

| | | | |
|---|---|---|---|
| Cu | 0.072300000 | -1.451000000 | 0.361700000 |
| O | -0.868400000 | -0.101700000 | 1.435000000 |
| O | 4.106500000 | 1.066800000 | -0.053500000 |
| N | 1.304400000 | -2.095700000 | 1.985600000 |
| N | 1.760400000 | -0.397600000 | -0.673700000 |
| N | -1.687800000 | -1.621400000 | -0.568400000 |
| N | 0.817800000 | -3.360800000 | -0.436400000 |
| C | 1.857300000 | -3.309000000 | 1.827000000 |
| C | -2.625800000 | -0.730700000 | -0.019300000 |

| | | | |
|---|---|---|---|
| C | -2.159900000 | -0.015300000 | 1.128200000 |
| C | -3.089100000 | 0.732000000 | 1.907500000 |
| C | 2.986300000 | -1.007700000 | -0.621800000 |
| C | 4.175400000 | -0.293600000 | -0.322900000 |
| C | -4.891900000 | 0.132100000 | 0.323800000 |
| C | 0.628300000 | 1.696600000 | -1.097100000 |
| C | 1.790000000 | 0.990600000 | -0.734500000 |
| C | 3.126700000 | -2.396800000 | -0.890900000 |
| C | 1.259500000 | -4.160000000 | 0.727300000 |
| C | -1.675600000 | -2.013500000 | -1.888400000 |
| C | -6.379200000 | 0.243900000 | -0.068600000 |
| C | -2.628600000 | 1.440800000 | 3.199500000 |
| C | -3.974400000 | -0.636700000 | -0.403100000 |
| C | 4.386700000 | -3.011900000 | -0.806500000 |
| C | 1.935600000 | -3.157700000 | -1.405600000 |
| C | 2.855300000 | -3.774200000 | 2.687300000 |
| C | 2.957400000 | 1.744600000 | -0.475900000 |
| C | 5.415600000 | -0.903900000 | -0.250300000 |
| C | 1.716300000 | -1.300800000 | 2.983700000 |
| C | 1.797600000 | 3.787200000 | -0.949400000 |
| C | 0.606900000 | 3.088300000 | -1.201800000 |
| C | -0.960900000 | -3.209200000 | -2.220200000 |
| C | -0.337500000 | -4.026400000 | -1.118800000 |
| C | 2.998400000 | 3.144000000 | -0.589900000 |
| C | -1.545500000 | 2.495000000 | 2.867900000 |
| C | -0.901200000 | -3.647000000 | -3.544300000 |
| C | -2.051300000 | 0.395800000 | 4.186200000 |
| C | -2.287800000 | -1.309600000 | -2.959200000 |
| C | 2.700400000 | -1.692500000 | 3.886300000 |
| C | 5.529000000 | -2.287300000 | -0.479100000 |
| C | -6.742600000 | 1.724300000 | -0.336100000 |
| C | -0.666300000 | 3.857300000 | -1.612200000 |
| C | -6.714200000 | -0.561100000 | -1.339300000 |
| C | -1.886200000 | 2.925600000 | -1.758500000 |
| C | -3.778500000 | 2.171700000 | 3.920700000 |
| C | -7.268000000 | -0.292300000 | 1.079300000 |
| C | 3.279700000 | -2.954500000 | 3.730700000 |
| C | -1.521500000 | -2.945000000 | -4.581600000 |
| C | -2.209800000 | -1.767700000 | -4.271000000 |
| C | 4.292200000 | 3.952100000 | -0.331700000 |
| C | -0.427600000 | 4.558400000 | -2.971300000 |
| C | 5.397000000 | 3.511000000 | -1.323300000 |
| C | 4.777600000 | 3.749400000 | 1.125000000 |
| C | -1.006500000 | 4.927400000 | -0.549000000 |
| C | 4.081100000 | 5.467900000 | -0.530200000 |
| C | -4.420100000 | 0.800500000 | 1.466400000 |
| H | -0.258000000 | 1.104000000 | -1.287900000 |

| | | | |
|---|---|---|---|
| H | 1.962400000 | -4.951000000 | 0.430500000 |
| H | 0.375100000 | -4.658300000 | 1.142600000 |
| H | -4.302900000 | -1.211900000 | -1.260000000 |
| H | 4.464400000 | -4.076500000 | -1.018700000 |
| H | 2.258800000 | -4.145300000 | -1.773900000 |
| H | 1.499100000 | -2.614300000 | -2.248500000 |
| H | 3.290700000 | -4.756300000 | 2.533700000 |
| H | 6.284100000 | -0.299900000 | -0.001100000 |
| H | 1.224300000 | -0.335100000 | 3.041400000 |
| H | 1.793300000 | 4.865500000 | -1.035500000 |
| H | -0.016200000 | -5.001500000 | -1.517500000 |
| H | -1.085000000 | -4.203700000 | -0.338100000 |
| H | -0.719000000 | 2.044000000 | 2.317400000 |
| H | -1.154900000 | 2.951200000 | 3.787200000 |
| H | -1.972000000 | 3.296800000 | 2.254200000 |
| H | -0.359500000 | -4.565000000 | -3.765400000 |
| H | -2.827000000 | -0.317200000 | 4.490100000 |
| H | -1.675800000 | 0.888800000 | 5.092400000 |
| H | -1.234400000 | -0.157100000 | 3.720100000 |
| H | -2.812700000 | -0.386000000 | -2.744600000 |
| H | 3.005300000 | -1.025200000 | 4.684900000 |
| H | 6.497400000 | -2.774000000 | -0.415200000 |
| H | -6.568900000 | 2.348100000 | 0.545900000 |
| H | -7.800200000 | 1.822000000 | -0.611700000 |
| H | -6.139100000 | 2.130600000 | -1.155100000 |
| H | -6.142200000 | -0.210700000 | -2.204700000 |
| H | -7.778300000 | -0.453800000 | -1.578100000 |
| H | -6.510700000 | -1.629200000 | -1.209400000 |
| H | -1.744100000 | 2.200700000 | -2.567200000 |
| H | -2.777500000 | 3.516600000 | -1.996900000 |
| H | -2.085700000 | 2.364000000 | -0.839300000 |
| H | -4.220200000 | 2.956000000 | 3.296600000 |
| H | -3.393200000 | 2.651000000 | 4.828100000 |
| H | -4.577300000 | 1.484800000 | 4.221300000 |
| H | -7.049700000 | -1.347100000 | 1.279600000 |
| H | -8.331000000 | -0.208700000 | 0.820600000 |
| H | -7.106000000 | 0.263000000 | 2.008000000 |
| H | 4.055400000 | -3.292800000 | 4.411000000 |
| H | -1.464700000 | -3.305300000 | -5.604400000 |
| H | -2.686400000 | -1.192800000 | -5.062300000 |
| H | 0.400000000 | 5.272900000 | -2.917400000 |
| H | -1.324300000 | 5.106300000 | -3.286200000 |
| H | -0.186800000 | 3.826800000 | -3.750100000 |
| H | 5.631200000 | 2.451300000 | -1.215800000 |
| H | 6.314700000 | 4.086700000 | -1.150300000 |
| H | 5.078700000 | 3.689200000 | -2.356600000 |
| H | 4.017000000 | 4.093800000 | 1.834700000 |

| | | | |
|---|---|---|---|
| H | 5.690200000 | 4.331500000 | 1.303600000 |
| H | 4.991400000 | 2.701300000 | 1.335700000 |
| H | -1.190000000 | 4.464200000 | 0.425400000 |
| H | -1.908400000 | 5.481300000 | -0.836500000 |
| H | -0.196500000 | 5.653100000 | -0.427000000 |
| H | 3.774200000 | 5.711600000 | -1.552700000 |
| H | 5.023100000 | 5.991900000 | -0.335200000 |
| H | 3.330600000 | 5.871900000 | 0.157300000 |
| H | -5.124900000 | 1.391200000 | 2.040100000 |

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