

Copper-Based Redox Shuttles Supported by Preorganized Tetradentate Ligands for Dye-Sensitized Solar Cells

Roberta R. Rodrigues, Joseph M. Lee, Natalie S. Taylor, Hammad Cheema, Lizhu Chen, Ryan C.
Fortenberry,* Jared H. Delcamp,* Jonah W. Jurss*

Department of Chemistry and Biochemistry, University of Mississippi, University, MS 38677-1848,
USA.

Table of Contents:

| | |
|---|-----|
| Figure S1: Calculated structure of $[\text{Cu}(\mathbf{1})(\text{MeCN})]^{1+}$ | S3 |
| Figure S2: UV-Vis spectra of $[\text{Cu}(\mathbf{3})]^{2+}$ | S3 |
| Figure S3: Cyclic voltammetry of $[\text{Cu}(\mathbf{2})]^{2+}$ and $[\text{Cu}(\mathbf{3})]^{2+}$ | S4 |
| Figure S4: <i>J-V</i> curves with PEDOT and Pt counter electrodes | S4 |
| Figure S5: Nyquist and Bode plots resulting from EIS measurements on DSC devices with PEDOT electrodes | S5 |
| Figure S6: EIS circuit used for all DSC graphs | S5 |
| Table S1: EIS data from PEDOT-based DSC devices | S5 |
| Figure S7: ^1H and ^{13}C NMR of 4-trifluoromethyl-2-amidrazone | S6 |
| Figure S8: ^1H (top) and ^{13}C NMR (bottom) of ligand 4 | S7 |
| Figure S9: ^1H NMR of $[\text{Cu}(\mathbf{3})]^+$ complex in CD_3CN | S8 |
| Figure S10: DSC devices prepared with dye Y123 with $[\text{Cu}(\text{bpye})_2]^{2+/1+}$ and $[\text{Cu}(\mathbf{1})]^{2+/1+}$ after 2 days for light soaking with indoor T8 lighting at about 10% sun intensity | S8 |
| Table S2: Crystallographic Data for $[\text{Cu}(\mathbf{1})(\text{MeCN})](\text{ClO}_4)_2$. | S9 |
| Table S3: Cartesian coordinates for optimized $[\text{Cu}(\mathbf{1})]^{1+}$ | S11 |
| Table S4: Cartesian coordinates for optimized $[\text{Cu}(\mathbf{1})]^{2+}$ | S12 |
| Table S5: Cartesian coordinates for optimized $[\text{Cu}(\mathbf{1})(\text{MeCN})]^{1+}$ | S13 |
| Table S6: Cartesian coordinates for optimized $[\text{Cu}(\mathbf{1})(\text{MeCN})]^{2+}$ | S15 |
| Table S7: Cartesian coordinates for optimized $[\text{Cu}(\mathbf{2})]^{1+}$ | S16 |
| Table S8: Cartesian coordinates for optimized $[\text{Cu}(\mathbf{2})]^{2+}$ | S18 |
| Table S9: Cartesian coordinates for optimized $[\text{Cu}(\mathbf{3})]^{1+}$ | S19 |
| Table S10: Cartesian coordinates for optimized $[\text{Cu}(\mathbf{3})]^{2+}$ | S21 |
| Table S11: Cartesian coordinates for optimized $[\text{Cu}(\text{bpye})_2]^{1+}$ | S22 |
| Table S12: Cartesian coordinates for optimized $[\text{Cu}(\text{bpye})_2]^{2+}$ | S24 |
| Table S13: Cartesian coordinates for optimized $[\text{Cu}(\text{dmby})_2]^{1+}$ | S25 |
| Table S14: Cartesian coordinates for optimized $[\text{Cu}(\text{dmby})_2]^{2+}$ | S26 |

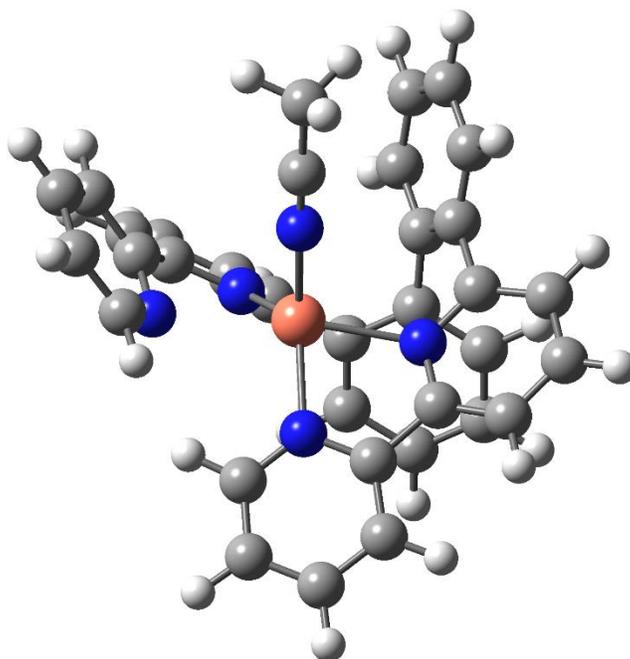


Figure S1. Calculated structure of $[\text{Cu}(\mathbf{1})(\text{MeCN})]^{1+}$ using the PBE1PBE (PBE0) functional and the 6-31G(d) basis set for all atoms except for Cu where the Def2TZVP basis set was employed. A polarizable continuum solvent model for acetonitrile was implemented within the Gaussian09 program.

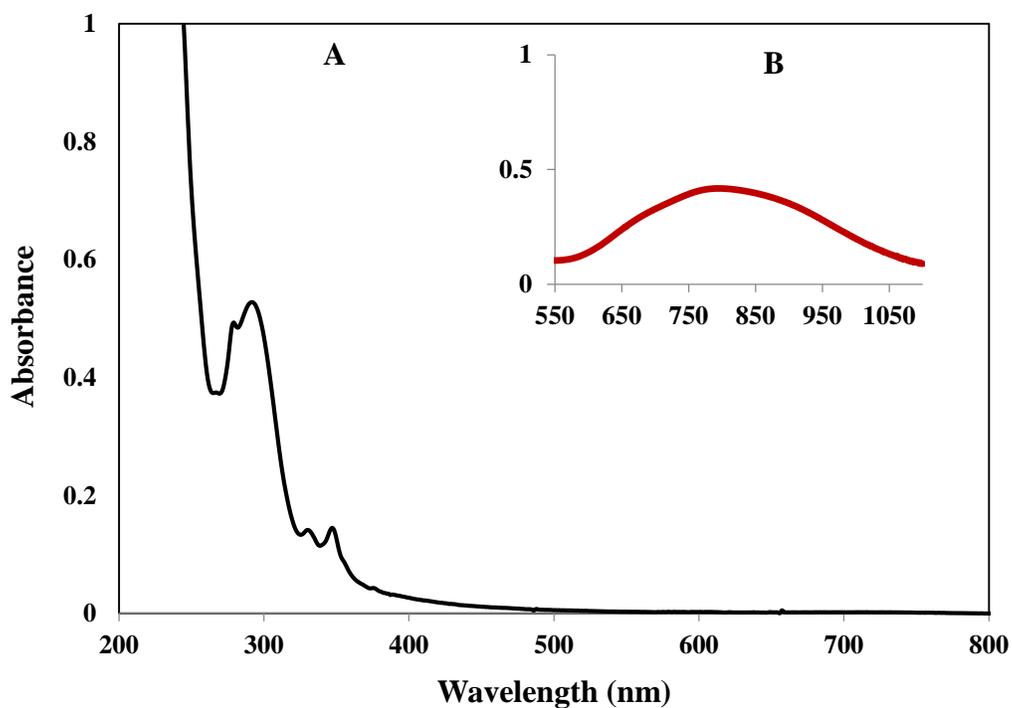


Figure S2. UV-vis spectra of $[\text{Cu}(\mathbf{3})]^{2+}$ at (A) 0.5 mM and (B) 60 mM concentrations in anhydrous acetonitrile. The molar absorptivity (ϵ) of the ligand-based transition at 292 nm and the d-d transition at 780 nm were found to be 7150 and 90 $\text{L mol}^{-1} \text{cm}^{-1}$, respectively.

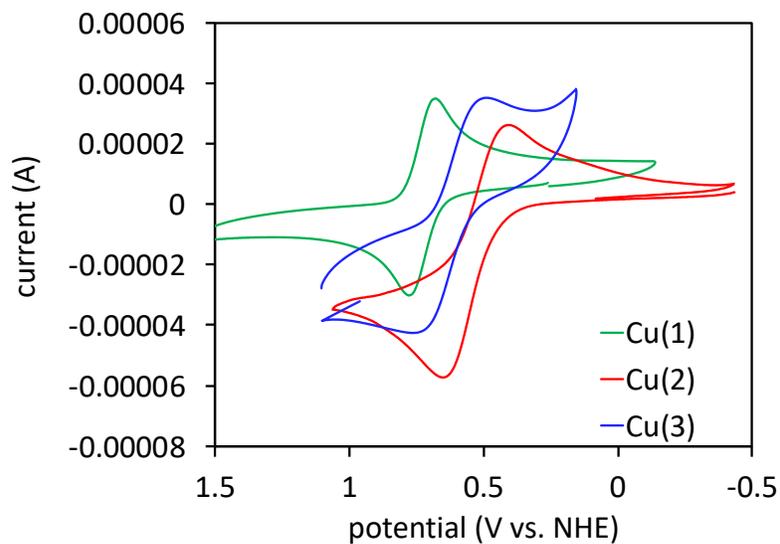


Figure S3. Cyclic voltammetry of 1 mM [Cu(1)]²⁺, [Cu(2)]²⁺, and [Cu(3)]²⁺ in anhydrous MeCN / 0.1 M Bu₄NPF₆. Glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode, $\nu = 100$ mV/s.

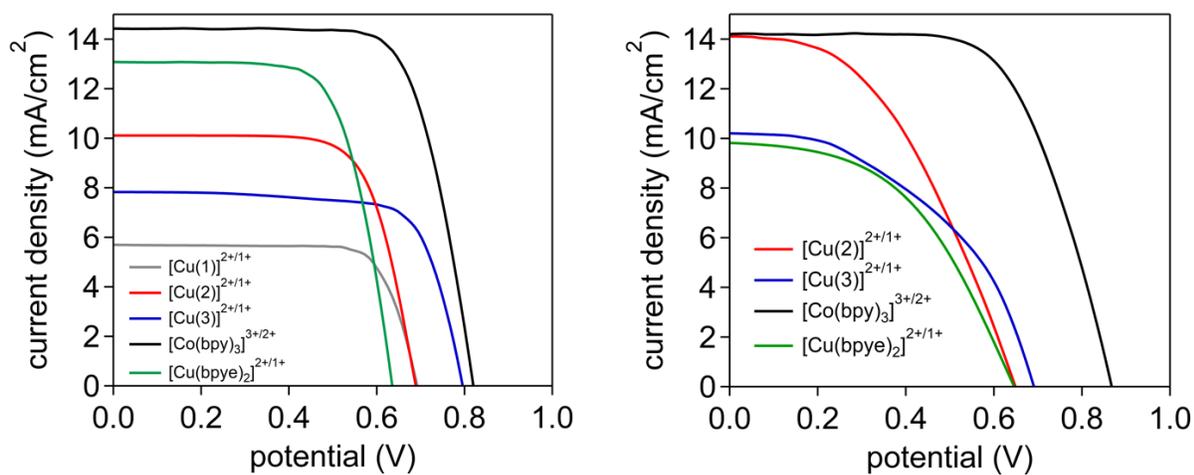


Figure S4. *J-V* curves with PEDOT counter electrode (left) and Pt counter electrode (right) for **Y123**/Cu shuttles-based DSC.

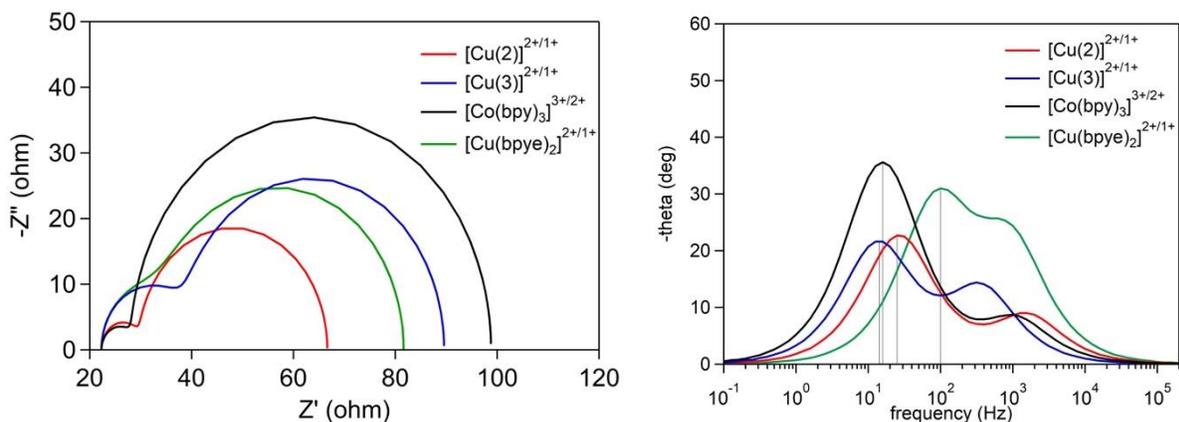


Figure S5. Nyquist (left) and Bode (right) plots resulting from EIS measurements on DSC devices with PEDOT electrodes.

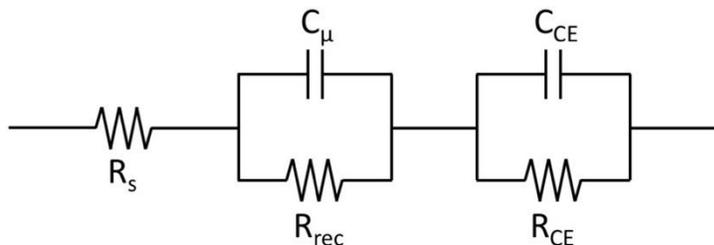


Figure S6. EIS circuit used for all DSC graphs.

Table S1. EIS data from PEDOT-based DSC devices.

| Entry | Redox Shuttle | R_s (Ω) | R_{rec} (Ω) | C_μ (mF) | R_{ce} (Ω) | C_{ce} (mF) | η_{cc} (%) | τ_{TiO_2} (ms) |
|-------|------------------------|--------------------|------------------------|----------------------|-----------------------|----------------------|-----------------|---------------------|
| 1 | $[Cu(2)]^{2+/1+}$ | 22 | 37 | 2.4×10^{-4} | 7 | 1.6×10^{-5} | 84 | 6 |
| 2 | $[Cu(3)]^{2+/1+}$ | 30 | 51 | 3.4×10^{-4} | 16 | 3.3×10^{-5} | 76 | 11 |
| 3 | $[Co(bpy)_3]^{3+/2+}$ | 20 | 71 | 2.8×10^{-4} | 6 | 2.8×10^{-5} | 92 | 10 |
| 4 | $[Cu(bpye)_2]^{2+/1+}$ | 14 | 48 | 6.3×10^{-3} | 12 | 1.2×10^{-3} | 80 | 1.6 |

R_s is the series resistance, R_{rec} is the recombination resistance of electrons in TiO_2 across the TiO_2 -dye interface to an oxidized redox shuttle, C_μ is the chemical capacitance for charge accumulation in TiO_2 , R_{CE} is the electron-transfer resistance at the counter electrode to an oxidized redox shuttle, and C_{CE} is the capacitance at the electrolyte-counter electrode interface. $\eta_{cc} = 1/(1 + (R_{CE}/R_{rec}))$, where η_{cc} is the charge collection efficiency. $\tau_{TiO_2} = 1/(2\pi f)$, where τ_{TiO_2} is the lifetime of injected electrons in TiO_2 and f is the peak frequency from the Bode plot for the lower frequency peak between 10 and 100 Hz (illustrated as gray lines in Figure S5).

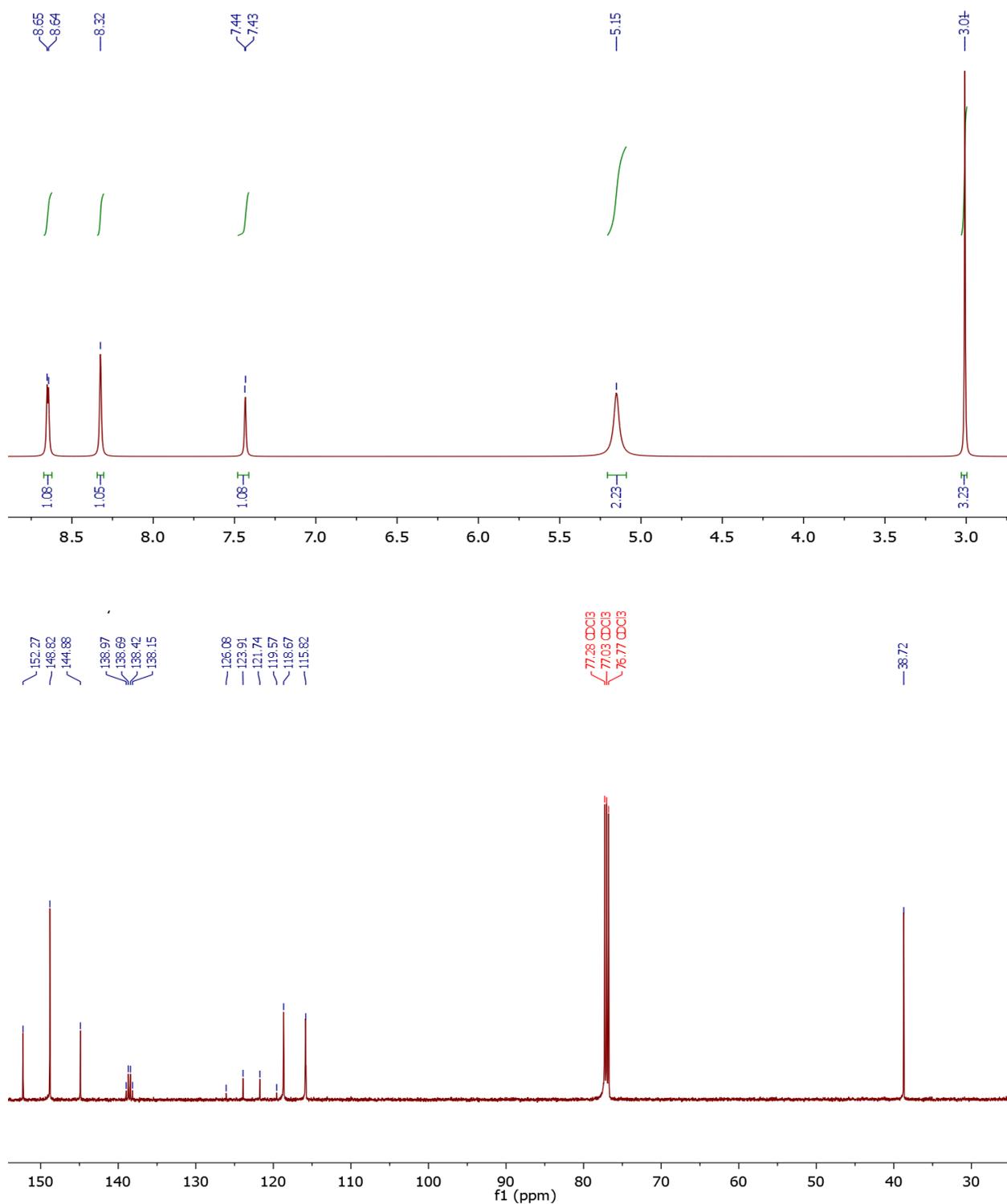


Figure S7. ^1H (top) and ^{13}C NMR (bottom) of 4-trifluoromethyl-2-amidrazone pyridine (**2**). Quartet splitting signals in the ^{13}C NMR are a result of the fluorinated carbon and adjacent carbon atom.

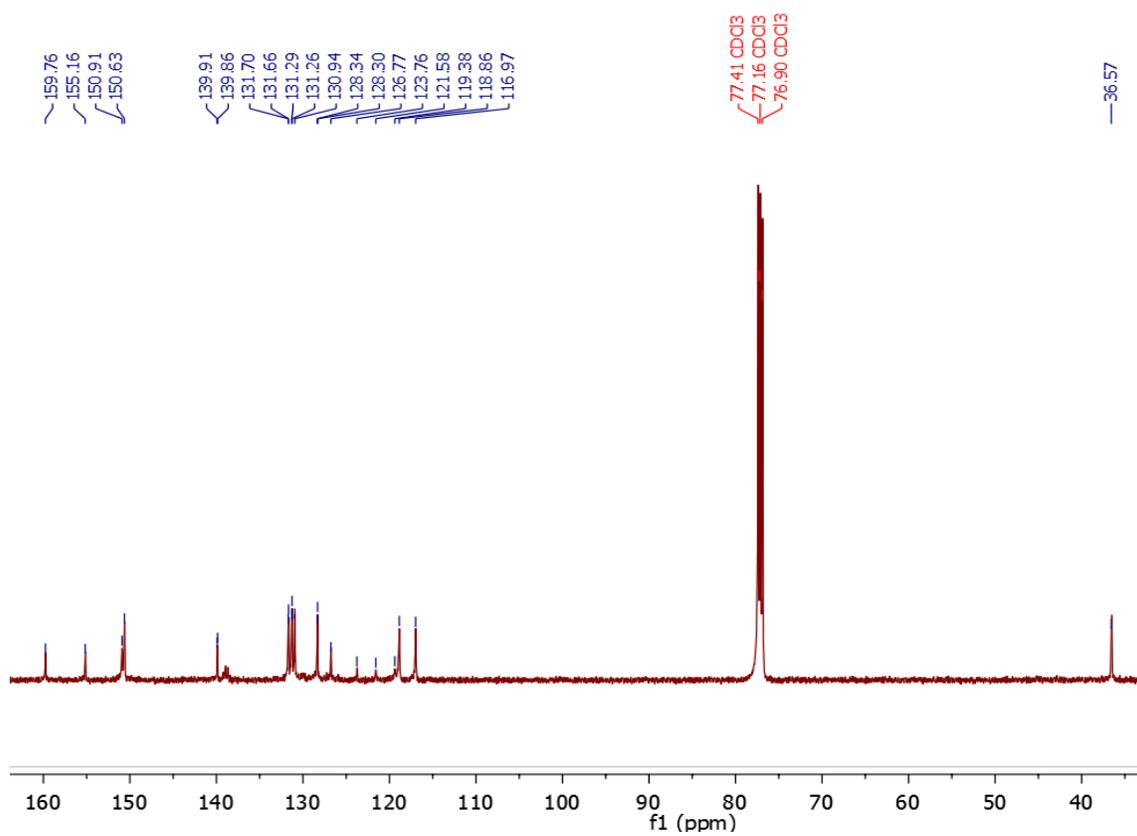
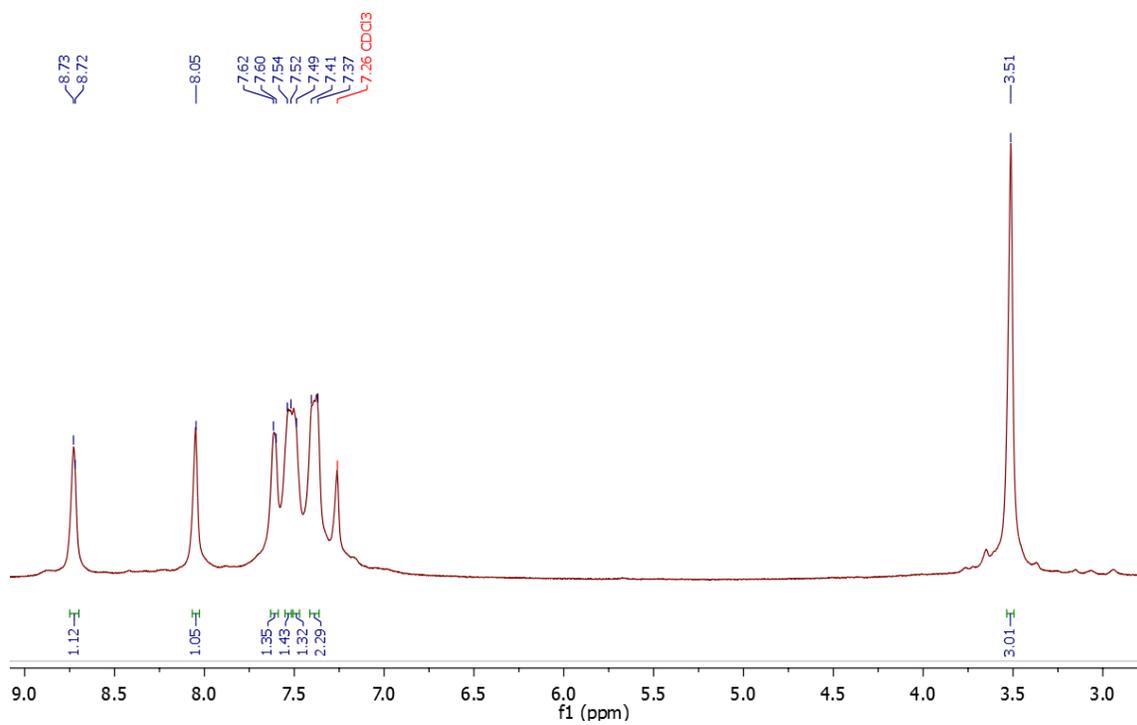


Figure S8. ^1H (top) and ^{13}C NMR (bottom) of ligand **4**. Quartet splitting signals are justified from the fluorinated carbon and adjacent carbon atom.

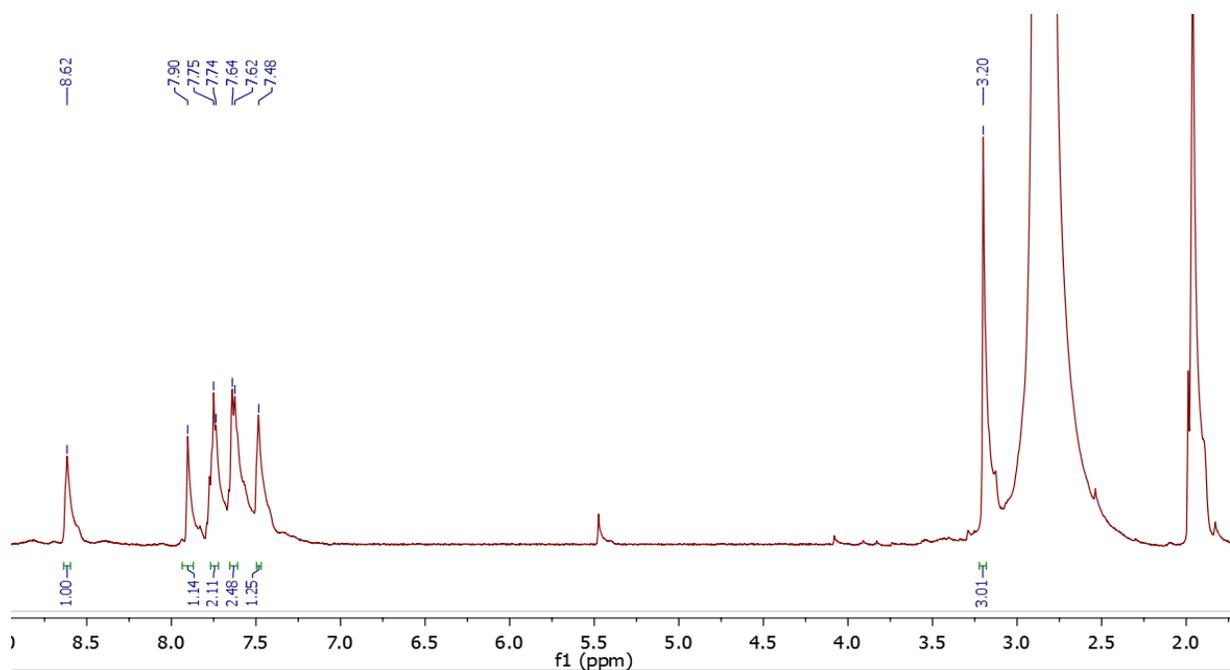


Figure S9. ^1H NMR of $[\text{Cu}(\mathbf{3})](\text{PF}_6)$ complex in CD_3CN . A small addition of hydrazine monohydrate was used to maintain a diamagnetic copper system.



Figure S10. DSC devices prepared with dye **Y123** with $[\text{Cu}(\text{bpye})_2]^{2+/1+}$ (left) and $[\text{Cu}(\mathbf{1})]^{2+/1+}$ (right) after 2 days for light soaking with indoor T8 lighting at about 10% sun intensity. A clear discoloration of the electrode is observed with a darkened electrolyte for $[\text{Cu}(\mathbf{1})]^{2+/1+}$ with both devices originally appearing near identical to the solar cell on the left.

Table S2. Crystallographic Data for [Cu(1)(MeCN)](ClO₄)₂.

| | |
|--|---|
| | Cu_LY2_0m |
| Crystal data | |
| Chemical formula | C ₃₄ H ₂₅ ClCuN ₅ O ₄ ·ClO ₄ ·C ₂ H ₅ N |
| M_r | 807.08 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 150 |
| a, b, c (Å) | 9.1754 (5), 13.2338 (14), 14.3608 (14) |
| α, β, γ (°) | 91.0207 (17), 91.024 (2), 91.5876 (16) |
| V (Å ³) | 1742.5 (3) |
| Z | 2 |
| $F(000)$ | 826 |
| D_x (Mg m ⁻³) | 1.538 |
| Radiation type | Mo $K\alpha$ |
| No. of reflections for cell measurement | 9932 |
| θ range (°) for cell measurement | 2.6–33.2 |
| μ (mm ⁻¹) | 0.84 |
| Crystal shape | Block |
| Colour | Blue |
| Crystal size (mm) | 0.60 × 0.45 × 0.30 |
| Data collection | |
| Diffractometer | Bruker AXS D8 Quest CMOS diffractometer |
| Radiation source | fine focus sealed tube X-ray source |
| Monochromator | Triumph curved graphite crystal |
| Detector resolution (pixels mm ⁻¹) | 10.4167 |
| Scan method | ω and phi scans |
| Absorption correction | Multi-scan, <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., <i>J. Appl. Cryst.</i> 48 (2015) 3-10 |
| T_{\min}, T_{\max} | 0.669, 0.747 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 67130, 13331, 11594 |
| R_{int} | 0.026 |
| θ values (°) | $\theta_{\max} = 33.2, \theta_{\min} = 2.6$ |
| $(\sin \theta/\lambda)_{\max}$ (Å ⁻¹) | 0.771 |
| Range of h, k, l | $h = -12 \rightarrow 14, k = -20 \rightarrow 20, l = -22 \rightarrow 21$ |

| Refinement | |
|---|---|
| Refinement on | F^2 |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ | 0.032, 0.089, 1.04 |
| No. of reflections | 13331 |
| No. of parameters | 527 |
| No. of restraints | 156 |
| H-atom treatment | H-atom parameters constrained |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 0.8541P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $(\Delta/\sigma)_{\max}$ | 0.004 |
| $\Delta\rho_{\max}, \Delta\rho_{\min}$ (e \AA^{-3}) | 0.48, -0.59 |
| Extinction method | <i>SHELXL2018/3</i> (Sheldrick 2018), $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ |
| Extinction coefficient | 0.0067 (8) |
| CCDC | 1959279 |

The perchlorate anion containing CL2 was refined as disordered over two components. Each component was restrained to have a similar geometry as the perchlorate containing CL1. Disordered atoms within 2 Å were restrained to have similar U^{ij} components. Under these conditions the occupancy for the major and minor moiety refined to 0.56(2) and 0.44(2), respectively.

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015, 2018), *SHELXLE* Rev955 (Hübschle *et al.*, 2011).

Table S3. Cartesian coordinates for optimized [Cu(1)]¹⁺.

| | | | |
|----|-----------|-----------|-----------|
| 29 | 0.000000 | 0.000000 | 0.740842 |
| 7 | -0.681147 | 1.589464 | 1.906529 |
| 6 | -1.577632 | 1.531089 | 2.894744 |
| 1 | -2.096721 | 0.584294 | 3.012287 |
| 6 | -1.847830 | 2.605083 | 3.733790 |
| 6 | -1.145398 | 3.788407 | 3.533207 |
| 6 | -0.210390 | 3.854880 | 2.507327 |
| 6 | 0.000000 | 2.733445 | 1.703312 |
| 6 | 0.962697 | 2.715765 | 0.573425 |
| 7 | 1.043031 | 1.554760 | -0.102300 |
| 6 | 1.847998 | 1.455005 | -1.171146 |
| 6 | 2.664499 | 2.514678 | -1.570087 |
| 6 | 2.607863 | 3.708040 | -0.861489 |
| 6 | 1.735708 | 3.819944 | 0.214050 |
| 1 | 1.666859 | 4.754151 | 0.758039 |
| 1 | 3.224659 | 4.552122 | -1.153825 |
| 1 | 3.310763 | 2.403133 | -2.434180 |
| 6 | 1.838441 | 0.166688 | -1.907298 |
| 6 | 0.644434 | -0.374933 | -2.428082 |
| 6 | 0.701165 | -1.616508 | -3.071195 |
| 6 | 1.900246 | -2.310384 | -3.203117 |
| 6 | 3.078216 | -1.762394 | -2.703262 |
| 6 | 3.042410 | -0.527430 | -2.063809 |
| 1 | 3.954809 | -0.100938 | -1.655085 |
| 1 | 4.020202 | -2.292969 | -2.806450 |
| 1 | 1.914205 | -3.271067 | -3.710015 |
| 1 | -0.209126 | -2.030896 | -3.496115 |
| 6 | -0.644434 | 0.374933 | -2.428082 |
| 6 | -1.838441 | -0.166688 | -1.907298 |
| 6 | -3.042410 | 0.527430 | -2.063809 |
| 6 | -3.078216 | 1.762394 | -2.703262 |
| 1 | -4.020202 | 2.292969 | -2.806450 |
| 6 | -1.900246 | 2.310384 | -3.203117 |
| 1 | -1.914205 | 3.271067 | -3.710015 |
| 6 | -0.701165 | 1.616508 | -3.071195 |
| 1 | 0.209126 | 2.030896 | -3.496115 |
| 1 | -3.954809 | 0.100938 | -1.655085 |
| 6 | -1.847998 | -1.455005 | -1.171146 |
| 7 | -1.043031 | -1.554760 | -0.102300 |
| 6 | -0.962697 | -2.715765 | 0.573425 |
| 6 | -1.735708 | -3.819944 | 0.214050 |
| 6 | -2.607863 | -3.708040 | -0.861489 |
| 6 | -2.664499 | -2.514678 | -1.570087 |

| | | | |
|---|-----------|-----------|-----------|
| 1 | -3.310763 | -2.403133 | -2.434180 |
| 1 | -3.224659 | -4.552122 | -1.153825 |
| 1 | -1.666859 | -4.754151 | 0.758039 |
| 6 | 0.000000 | -2.733445 | 1.703312 |
| 7 | 0.681147 | -1.589464 | 1.906529 |
| 6 | 1.577632 | -1.531089 | 2.894744 |
| 1 | 2.096721 | -0.584294 | 3.012287 |
| 6 | 1.847830 | -2.605083 | 3.733790 |
| 6 | 1.145398 | -3.788407 | 3.533207 |
| 6 | 0.210390 | -3.854880 | 2.507327 |
| 1 | -0.343780 | -4.771591 | 2.344114 |
| 1 | 1.320648 | -4.652427 | 4.166586 |
| 1 | 2.588173 | -2.509426 | 4.520616 |
| 1 | 0.343780 | 4.771591 | 2.344114 |
| 1 | -1.320648 | 4.652427 | 4.166586 |
| 1 | -2.588173 | 2.509426 | 4.520616 |

Table S4. Cartesian coordinates for optimized [Cu(1)]²⁺.

| | | | |
|----|-----------|-----------|-----------|
| 29 | 0.000000 | 0.000000 | 0.828183 |
| 7 | -0.411518 | 1.459826 | 2.103094 |
| 6 | -1.194462 | 1.318644 | 3.177231 |
| 1 | -1.488827 | 0.306407 | 3.434254 |
| 6 | -1.608119 | 2.411750 | 3.925343 |
| 6 | -1.195175 | 3.679418 | 3.529834 |
| 6 | -0.382928 | 3.819226 | 2.409325 |
| 6 | 0.000000 | 2.680296 | 1.708809 |
| 6 | 0.869940 | 2.684996 | 0.518149 |
| 7 | 0.920269 | 1.521266 | -0.168332 |
| 6 | 1.750954 | 1.398852 | -1.218847 |
| 6 | 2.569862 | 2.459523 | -1.612844 |
| 6 | 2.506691 | 3.662437 | -0.926553 |
| 6 | 1.640939 | 3.781877 | 0.154311 |
| 1 | 1.595277 | 4.703552 | 0.721322 |
| 1 | 3.128313 | 4.500561 | -1.224002 |
| 1 | 3.229198 | 2.330111 | -2.463655 |
| 6 | 1.787653 | 0.112776 | -1.951244 |
| 6 | 0.635653 | -0.386454 | -2.581655 |
| 6 | 0.715673 | -1.605581 | -3.261177 |
| 6 | 1.911898 | -2.314104 | -3.319395 |
| 6 | 3.053976 | -1.807593 | -2.703358 |
| 6 | 2.992287 | -0.594112 | -2.027019 |
| 1 | 3.876728 | -0.197160 | -1.536299 |
| 1 | 3.990720 | -2.354723 | -2.748138 |

| | | | |
|---|-----------|-----------|-----------|
| 1 | 1.953413 | -3.257437 | -3.855951 |
| 1 | -0.166561 | -1.988938 | -3.766401 |
| 6 | -0.635653 | 0.386454 | -2.581655 |
| 6 | -1.787653 | -0.112776 | -1.951244 |
| 6 | -2.992287 | 0.594112 | -2.027019 |
| 6 | -3.053976 | 1.807593 | -2.703358 |
| 1 | -3.990720 | 2.354723 | -2.748138 |
| 6 | -1.911898 | 2.314104 | -3.319395 |
| 1 | -1.953413 | 3.257437 | -3.855951 |
| 6 | -0.715673 | 1.605581 | -3.261177 |
| 1 | 0.166561 | 1.988938 | -3.766401 |
| 1 | -3.876728 | 0.197160 | -1.536299 |
| 6 | -1.750954 | -1.398852 | -1.218847 |
| 7 | -0.920269 | -1.521266 | -0.168332 |
| 6 | -0.869940 | -2.684996 | 0.518149 |
| 6 | -1.640939 | -3.781877 | 0.154311 |
| 6 | -2.506691 | -3.662437 | -0.926553 |
| 6 | -2.569862 | -2.459523 | -1.612844 |
| 1 | -3.229198 | -2.330111 | -2.463655 |
| 1 | -3.128313 | -4.500561 | -1.224002 |
| 1 | -1.595277 | -4.703552 | 0.721322 |
| 6 | 0.000000 | -2.680296 | 1.708809 |
| 7 | 0.411518 | -1.459826 | 2.103094 |
| 6 | 1.194462 | -1.318644 | 3.177231 |
| 1 | 1.488827 | -0.306407 | 3.434254 |
| 6 | 1.608119 | -2.411750 | 3.925343 |
| 6 | 1.195175 | -3.679418 | 3.529834 |
| 6 | 0.382928 | -3.819226 | 2.409325 |
| 1 | 0.068021 | -4.802834 | 2.082328 |
| 1 | 1.504639 | -4.558010 | 4.086326 |
| 1 | 2.240724 | -2.263824 | 4.792768 |
| 1 | -0.068021 | 4.802834 | 2.082328 |
| 1 | -1.504639 | 4.558010 | 4.086326 |
| 1 | -2.240724 | 2.263824 | 4.792768 |

Table S5. Cartesian coordinates for optimized [Cu(**1**)(MeCN)]¹⁺.

| | | | |
|----|-----------|----------|-----------|
| 29 | 0.335486 | 0.583604 | 0.111719 |
| 7 | -0.484450 | 2.454516 | -0.394171 |
| 6 | 0.119124 | 3.345501 | -1.185461 |
| 1 | 1.126925 | 3.082152 | -1.494745 |
| 6 | -0.485649 | 4.530749 | -1.587040 |
| 1 | 0.047035 | 5.223629 | -2.229637 |
| 6 | -1.779325 | 4.793144 | -1.148382 |

| | | | |
|---|-----------|-----------|-----------|
| 1 | -2.293975 | 5.701494 | -1.446367 |
| 6 | -2.412852 | 3.868967 | -0.326148 |
| 1 | -3.429148 | 4.044096 | 0.008520 |
| 6 | -1.733403 | 2.705788 | 0.039197 |
| 6 | -2.336479 | 1.666610 | 0.909259 |
| 7 | -1.740274 | 0.467362 | 0.867415 |
| 6 | -2.212642 | -0.538370 | 1.616240 |
| 6 | -3.303753 | -0.364681 | 2.471535 |
| 6 | -3.915110 | 0.882033 | 2.530831 |
| 6 | -3.434103 | 1.915468 | 1.736130 |
| 1 | -3.890432 | 2.897857 | 1.781004 |
| 1 | -4.763061 | 1.047691 | 3.188410 |
| 1 | -3.671551 | -1.198140 | 3.061045 |
| 6 | -1.509255 | -1.838392 | 1.498938 |
| 6 | -1.098032 | -2.499307 | 2.660384 |
| 1 | -1.332747 | -2.064205 | 3.628532 |
| 6 | -0.361691 | -3.677783 | 2.589933 |
| 1 | -0.041528 | -4.172907 | 3.502210 |
| 6 | -0.031977 | -4.209132 | 1.345849 |
| 1 | 0.542007 | -5.128890 | 1.277161 |
| 6 | -0.458718 | -3.571982 | 0.183872 |
| 1 | -0.237321 | -4.013109 | -0.784193 |
| 6 | -1.203144 | -2.389076 | 0.237204 |
| 6 | -1.763933 | -1.816298 | -1.017162 |
| 6 | -3.156516 | -1.727190 | -1.140699 |
| 1 | -3.776823 | -2.041016 | -0.305383 |
| 6 | -3.755703 | -1.267881 | -2.307871 |
| 1 | -4.838675 | -1.212704 | -2.373548 |
| 6 | -2.964173 | -0.895106 | -3.390944 |
| 1 | -3.418494 | -0.537023 | -4.310180 |
| 6 | -1.580628 | -0.989473 | -3.290071 |
| 1 | -0.955143 | -0.698903 | -4.130191 |
| 6 | -0.968153 | -1.436725 | -2.112671 |
| 6 | 0.518240 | -1.504234 | -2.110189 |
| 7 | 1.211555 | -0.681703 | -1.301608 |
| 6 | 2.559149 | -0.697280 | -1.369724 |
| 6 | 3.252986 | -1.551112 | -2.226263 |
| 6 | 2.538144 | -2.408056 | -3.051677 |
| 6 | 1.152454 | -2.375782 | -2.999747 |
| 1 | 0.550682 | -3.019129 | -3.632806 |
| 1 | 3.052909 | -3.077816 | -3.733613 |
| 1 | 4.336254 | -1.517010 | -2.265097 |
| 6 | 3.301574 | 0.271421 | -0.524745 |
| 7 | 2.734073 | 1.474519 | -0.362722 |

| | | | |
|---|----------|-----------|-----------|
| 6 | 3.376349 | 2.377422 | 0.378416 |
| 6 | 4.600880 | 2.135735 | 0.995357 |
| 6 | 5.183057 | 0.883336 | 0.831501 |
| 6 | 4.525780 | -0.066554 | 0.056759 |
| 1 | 4.943755 | -1.059469 | -0.073716 |
| 1 | 6.131551 | 0.644734 | 1.303427 |
| 1 | 5.078426 | 2.909452 | 1.587649 |
| 1 | 2.886297 | 3.343433 | 0.483458 |
| 7 | 1.164130 | 0.222611 | 1.937927 |
| 6 | 1.627604 | -0.077224 | 2.954201 |
| 6 | 2.205041 | -0.464928 | 4.225957 |
| 1 | 1.820578 | -1.446069 | 4.519727 |
| 1 | 1.943467 | 0.267109 | 4.995128 |
| 1 | 3.293836 | -0.518561 | 4.138851 |

Table S6. Cartesian coordinates for optimized $[\text{Cu}(\mathbf{1})(\text{MeCN})]^{2+}$.

| | | | |
|----|-----------|-----------|-----------|
| 29 | -0.559733 | 0.471673 | -0.439069 |
| 7 | -0.388371 | 2.426407 | 0.050590 |
| 6 | -1.272608 | 3.141643 | 0.750486 |
| 1 | -2.151411 | 2.613326 | 1.102887 |
| 6 | -1.083657 | 4.491362 | 1.014726 |
| 1 | -1.822711 | 5.037294 | 1.589696 |
| 6 | 0.062849 | 5.107627 | 0.526634 |
| 1 | 0.245955 | 6.161039 | 0.711887 |
| 6 | 0.985509 | 4.358678 | -0.195171 |
| 1 | 1.894806 | 4.819957 | -0.560921 |
| 6 | 0.732641 | 3.008085 | -0.416874 |
| 6 | 1.663855 | 2.101265 | -1.114600 |
| 7 | 1.391578 | 0.785502 | -0.981829 |
| 6 | 2.237904 | -0.129936 | -1.490782 |
| 6 | 3.340581 | 0.262704 | -2.252644 |
| 6 | 3.590944 | 1.613042 | -2.445474 |
| 6 | 2.758166 | 2.550050 | -1.845820 |
| 1 | 2.951187 | 3.609442 | -1.962423 |
| 1 | 4.442137 | 1.936927 | -3.035451 |
| 1 | 4.003247 | -0.495260 | -2.655409 |
| 6 | 1.998694 | -1.555631 | -1.181353 |
| 6 | 1.935873 | -2.491546 | -2.218509 |
| 1 | 2.074677 | -2.160244 | -3.244414 |
| 6 | 1.653725 | -3.825530 | -1.948476 |
| 1 | 1.597654 | -4.543558 | -2.761382 |
| 6 | 1.437268 | -4.232574 | -0.632998 |
| 1 | 1.212532 | -5.272169 | -0.413211 |

| | | | |
|---|-----------|-----------|-----------|
| 6 | 1.545729 | -3.315109 | 0.407317 |
| 1 | 1.439547 | -3.649205 | 1.435741 |
| 6 | 1.843694 | -1.971728 | 0.154969 |
| 6 | 2.155162 | -1.055887 | 1.286644 |
| 6 | 3.455760 | -0.544197 | 1.384510 |
| 1 | 4.179415 | -0.796570 | 0.614227 |
| 6 | 3.841895 | 0.250107 | 2.458093 |
| 1 | 4.858062 | 0.630098 | 2.509906 |
| 6 | 2.929305 | 0.540146 | 3.469053 |
| 1 | 3.219998 | 1.155841 | 4.314973 |
| 6 | 1.637000 | 0.034163 | 3.390668 |
| 1 | 0.916102 | 0.262883 | 4.171116 |
| 6 | 1.236686 | -0.751961 | 2.303177 |
| 6 | -0.170991 | -1.224222 | 2.292387 |
| 7 | -1.001046 | -0.762502 | 1.345825 |
| 6 | -2.310885 | -1.073636 | 1.410512 |
| 6 | -2.821729 | -1.919797 | 2.391844 |
| 6 | -1.957383 | -2.432379 | 3.350367 |
| 6 | -0.621320 | -2.064749 | 3.314890 |
| 1 | 0.081048 | -2.420334 | 4.060758 |
| 1 | -2.329325 | -3.095314 | 4.124923 |
| 1 | -3.875350 | -2.166508 | 2.427002 |
| 6 | -3.186668 | -0.400818 | 0.423908 |
| 7 | -2.586656 | 0.488456 | -0.387120 |
| 6 | -3.298256 | 1.185582 | -1.278343 |
| 6 | -4.670466 | 1.032183 | -1.407027 |
| 6 | -5.307436 | 0.107637 | -0.586141 |
| 6 | -4.562238 | -0.614444 | 0.337689 |
| 1 | -5.054465 | -1.333334 | 0.980521 |
| 1 | -6.378335 | -0.051572 | -0.660318 |
| 1 | -5.215909 | 1.619993 | -2.136244 |
| 1 | -2.745322 | 1.881460 | -1.901491 |
| 7 | -0.855396 | -0.895732 | -1.957889 |
| 6 | -1.195176 | -1.604440 | -2.802746 |
| 6 | -1.603367 | -2.498864 | -3.862892 |
| 1 | -0.795148 | -3.204612 | -4.075124 |
| 1 | -1.828078 | -1.922358 | -4.764561 |
| 1 | -2.495204 | -3.051599 | -3.554879 |

Table S7. Cartesian coordinates for optimized [Cu(2)]¹⁺.

| | | | |
|----|-----------|----------|----------|
| 29 | 0.000000 | 0.000000 | 1.382760 |
| 7 | -1.277060 | 1.285062 | 2.453269 |
| 6 | -1.839120 | 1.064911 | 3.646407 |

| | | | |
|---|-----------|-----------|-----------|
| 1 | -1.693160 | 0.074324 | 4.066596 |
| 6 | -2.574936 | 2.030228 | 4.324350 |
| 6 | -2.733199 | 3.283179 | 3.738619 |
| 6 | -2.149652 | 3.526585 | 2.501162 |
| 6 | -1.429458 | 2.502672 | 1.893111 |
| 6 | -0.784354 | 2.650471 | 0.588451 |
| 7 | -0.907101 | 3.674118 | -0.237639 |
| 7 | -0.169149 | 3.295969 | -1.295259 |
| 6 | 0.365858 | 2.074169 | -1.091093 |
| 7 | 0.000000 | 1.653653 | 0.111982 |
| 6 | 1.224958 | 1.314115 | -2.017409 |
| 6 | 0.724229 | 0.180332 | -2.685886 |
| 6 | 1.609689 | -0.582959 | -3.452854 |
| 6 | 2.951573 | -0.230060 | -3.568477 |
| 6 | 3.433382 | 0.903989 | -2.921482 |
| 6 | 2.571162 | 1.669943 | -2.143759 |
| 1 | 2.944265 | 2.541029 | -1.612389 |
| 1 | 4.477333 | 1.188058 | -3.012039 |
| 1 | 3.616866 | -0.838064 | -4.174516 |
| 1 | 1.232537 | -1.450347 | -3.987579 |
| 6 | -0.724229 | -0.180332 | -2.685886 |
| 6 | -1.224958 | -1.314115 | -2.017409 |
| 6 | -2.571162 | -1.669943 | -2.143759 |
| 6 | -3.433382 | -0.903989 | -2.921482 |
| 1 | -4.477333 | -1.188058 | -3.012039 |
| 6 | -2.951573 | 0.230060 | -3.568477 |
| 1 | -3.616866 | 0.838064 | -4.174516 |
| 6 | -1.609689 | 0.582959 | -3.452854 |
| 1 | -1.232537 | 1.450347 | -3.987579 |
| 1 | -2.944265 | -2.541029 | -1.612389 |
| 6 | -0.365858 | -2.074169 | -1.091093 |
| 7 | 0.000000 | -1.653653 | 0.111982 |
| 6 | 0.784354 | -2.650471 | 0.588451 |
| 6 | 1.429458 | -2.502672 | 1.893111 |
| 7 | 1.277060 | -1.285062 | 2.453269 |
| 6 | 1.839120 | -1.064911 | 3.646407 |
| 1 | 1.693160 | -0.074324 | 4.066596 |
| 6 | 2.574936 | -2.030228 | 4.324350 |
| 6 | 2.733199 | -3.283179 | 3.738619 |
| 6 | 2.149652 | -3.526585 | 2.501162 |
| 1 | 2.241384 | -4.487422 | 2.006157 |
| 1 | 3.301148 | -4.061166 | 4.239214 |
| 1 | 3.013243 | -1.797670 | 5.288803 |
| 7 | 0.907101 | -3.674118 | -0.237639 |

| | | | |
|---|-----------|-----------|-----------|
| 7 | 0.169149 | -3.295969 | -1.295259 |
| 6 | 0.065307 | -4.156564 | -2.455035 |
| 1 | -0.607598 | -3.690636 | -3.174682 |
| 1 | 1.053021 | -4.289660 | -2.901477 |
| 1 | -0.335882 | -5.125067 | -2.151220 |
| 6 | -0.065307 | 4.156564 | -2.455035 |
| 1 | 0.607598 | 3.690636 | -3.174682 |
| 1 | -1.053021 | 4.289660 | -2.901477 |
| 1 | 0.335882 | 5.125067 | -2.151220 |
| 1 | -2.241384 | 4.487422 | 2.006157 |
| 1 | -3.301148 | 4.061166 | 4.239214 |
| 1 | -3.013243 | 1.797670 | 5.288803 |

Table S8. Cartesian coordinates for optimized $[\text{Cu}(2)]^{2+}$.

| | | | |
|----|-----------|-----------|-----------|
| 29 | 0.000000 | 0.000000 | 1.224450 |
| 7 | -0.908129 | 1.312829 | 2.475839 |
| 6 | -1.408879 | 1.045124 | 3.686144 |
| 1 | -1.254867 | 0.040832 | 4.065982 |
| 6 | -2.098220 | 2.000047 | 4.422878 |
| 6 | -2.272479 | 3.269708 | 3.881225 |
| 6 | -1.766815 | 3.547021 | 2.615093 |
| 6 | -1.095250 | 2.539091 | 1.940105 |
| 6 | -0.527673 | 2.672611 | 0.604558 |
| 7 | -0.398330 | 3.756403 | -0.124963 |
| 7 | 0.254618 | 3.313356 | -1.215618 |
| 6 | 0.509975 | 1.996749 | -1.133876 |
| 7 | 0.000000 | 1.566585 | 0.021250 |
| 6 | 1.306751 | 1.196154 | -2.074542 |
| 6 | 0.733819 | 0.125140 | -2.780228 |
| 6 | 1.565144 | -0.674939 | -3.567921 |
| 6 | 2.928624 | -0.410451 | -3.666409 |
| 6 | 3.484190 | 0.666934 | -2.981916 |
| 6 | 2.675359 | 1.466907 | -2.182647 |
| 1 | 3.107080 | 2.290979 | -1.621700 |
| 1 | 4.545500 | 0.880624 | -3.059932 |
| 1 | 3.554830 | -1.042947 | -4.288420 |
| 1 | 1.129672 | -1.498194 | -4.127263 |
| 6 | -0.733819 | -0.125140 | -2.780228 |
| 6 | -1.306751 | -1.196154 | -2.074542 |
| 6 | -2.675359 | -1.466907 | -2.182647 |
| 6 | -3.484190 | -0.666934 | -2.981916 |
| 1 | -4.545500 | -0.880624 | -3.059932 |
| 6 | -2.928624 | 0.410451 | -3.666409 |

| | | | |
|---|-----------|-----------|-----------|
| 1 | -3.554830 | 1.042947 | -4.288420 |
| 6 | -1.565144 | 0.674939 | -3.567921 |
| 1 | -1.129672 | 1.498194 | -4.127263 |
| 1 | -3.107080 | -2.290979 | -1.621700 |
| 6 | -0.509975 | -1.996749 | -1.133876 |
| 7 | 0.000000 | -1.566585 | 0.021250 |
| 6 | 0.527673 | -2.672611 | 0.604558 |
| 6 | 1.095250 | -2.539091 | 1.940105 |
| 7 | 0.908129 | -1.312829 | 2.475839 |
| 6 | 1.408879 | -1.045124 | 3.686144 |
| 1 | 1.254867 | -0.040832 | 4.065982 |
| 6 | 2.098220 | -2.000047 | 4.422878 |
| 6 | 2.272479 | -3.269708 | 3.881225 |
| 6 | 1.766815 | -3.547021 | 2.615093 |
| 1 | 1.890737 | -4.517555 | 2.147953 |
| 1 | 2.803498 | -4.036779 | 4.435277 |
| 1 | 2.486960 | -1.743662 | 5.401530 |
| 7 | 0.398330 | -3.756403 | -0.124963 |
| 7 | -0.254618 | -3.313356 | -1.215618 |
| 6 | -0.574762 | -4.236725 | -2.287936 |
| 1 | -1.030131 | -3.677733 | -3.104196 |
| 1 | 0.346305 | -4.711844 | -2.628372 |
| 1 | -1.270500 | -4.991790 | -1.918116 |
| 6 | 0.574762 | 4.236725 | -2.287936 |
| 1 | 1.030131 | 3.677733 | -3.104196 |
| 1 | -0.346305 | 4.711844 | -2.628372 |
| 1 | 1.270500 | 4.991790 | -1.918116 |
| 1 | -1.890737 | 4.517555 | 2.147953 |
| 1 | -2.803498 | 4.036779 | 4.435277 |
| 1 | -2.486960 | 1.743662 | 5.401530 |

Table S9. Cartesian coordinates for optimized $[\text{Cu}(\mathbf{3})]^{1+}$.

| | | | |
|----|-----------|-----------|-----------|
| 29 | 0.000000 | 0.000000 | -0.474331 |
| 7 | -0.291496 | -1.784852 | -1.559600 |
| 6 | -0.885311 | -1.929180 | -2.748434 |
| 1 | -1.358030 | -1.043247 | -3.159998 |
| 6 | -0.916826 | -3.135903 | -3.434853 |
| 6 | -0.297150 | -4.240708 | -2.856569 |
| 6 | 0.326518 | -4.107964 | -1.624174 |
| 6 | 0.307183 | -2.859406 | -1.009621 |
| 6 | 0.922023 | -2.609172 | 0.292340 |
| 7 | 1.439343 | -3.512865 | 1.104612 |
| 7 | 1.815501 | -2.780225 | 2.165378 |

| | | | |
|---|-----------|-----------|-----------|
| 6 | 1.516652 | -1.477337 | 1.976726 |
| 7 | 0.962467 | -1.346511 | 0.779155 |
| 6 | 1.766066 | -0.361849 | 2.906854 |
| 6 | 0.694198 | 0.274275 | 3.562617 |
| 6 | 0.966988 | 1.412974 | 4.326800 |
| 6 | 2.264198 | 1.902697 | 4.453459 |
| 6 | 3.320534 | 1.253051 | 3.821917 |
| 6 | 3.068761 | 0.126368 | 3.046027 |
| 1 | 3.882290 | -0.370728 | 2.525026 |
| 1 | 4.335411 | 1.625313 | 3.922356 |
| 1 | 2.448401 | 2.786261 | 5.057525 |
| 1 | 0.152105 | 1.903175 | 4.852367 |
| 6 | -0.694198 | -0.274275 | 3.562617 |
| 6 | -1.766066 | 0.361849 | 2.906854 |
| 6 | -3.068761 | -0.126368 | 3.046027 |
| 6 | -3.320534 | -1.253051 | 3.821917 |
| 1 | -4.335411 | -1.625313 | 3.922356 |
| 6 | -2.264198 | -1.902697 | 4.453459 |
| 1 | -2.448401 | -2.786261 | 5.057525 |
| 6 | -0.966988 | -1.412974 | 4.326800 |
| 1 | -0.152105 | -1.903175 | 4.852367 |
| 1 | -3.882290 | 0.370728 | 2.525026 |
| 6 | -1.516652 | 1.477337 | 1.976726 |
| 7 | -0.962467 | 1.346511 | 0.779155 |
| 6 | -0.922023 | 2.609172 | 0.292340 |
| 6 | -0.307183 | 2.859406 | -1.009621 |
| 7 | 0.291496 | 1.784852 | -1.559600 |
| 6 | 0.885311 | 1.929180 | -2.748434 |
| 1 | 1.358030 | 1.043247 | -3.159998 |
| 6 | 0.916826 | 3.135903 | -3.434853 |
| 6 | 0.297150 | 4.240708 | -2.856569 |
| 6 | -0.326518 | 4.107964 | -1.624174 |
| 1 | -0.816748 | 4.944391 | -1.139372 |
| 6 | 0.270932 | 5.553813 | -3.592410 |
| 9 | 0.000000 | 6.577739 | -2.774316 |
| 9 | 1.446008 | 5.800487 | -4.187147 |
| 9 | -0.666576 | 5.543560 | -4.552210 |
| 1 | 1.421127 | 3.205683 | -4.392084 |
| 7 | -1.439343 | 3.512865 | 1.104612 |
| 7 | -1.815501 | 2.780225 | 2.165378 |
| 6 | -2.420607 | 3.421262 | 3.314619 |
| 1 | -2.689029 | 2.653186 | 4.039508 |
| 1 | -1.709071 | 4.120162 | 3.759067 |
| 1 | -3.316831 | 3.957363 | 2.997848 |

| | | | |
|---|-----------|-----------|-----------|
| 6 | 2.420607 | -3.421262 | 3.314619 |
| 1 | 2.689029 | -2.653186 | 4.039508 |
| 1 | 1.709071 | -4.120162 | 3.759067 |
| 1 | 3.316831 | -3.957363 | 2.997848 |
| 1 | 0.816748 | -4.944391 | -1.139372 |
| 6 | -0.270932 | -5.553813 | -3.592410 |
| 9 | 0.000000 | -6.577739 | -2.774316 |
| 9 | -1.446008 | -5.800487 | -4.187147 |
| 9 | 0.666576 | -5.543560 | -4.552210 |
| 1 | -1.421127 | -3.205683 | -4.392084 |

Table S10. Cartesian coordinates for optimized [Cu(3)]²⁺.

| | | | |
|----|-----------|-----------|-----------|
| 29 | 0.000000 | 0.000000 | -0.292563 |
| 7 | -0.028628 | -1.602541 | -1.550597 |
| 6 | -0.595168 | -1.662665 | -2.758166 |
| 1 | -1.041358 | -0.750665 | -3.138966 |
| 6 | -0.623833 | -2.837003 | -3.499689 |
| 6 | -0.046250 | -3.978608 | -2.956503 |
| 6 | 0.523924 | -3.930256 | -1.689331 |
| 6 | 0.509105 | -2.719270 | -1.015086 |
| 6 | 1.054253 | -2.513218 | 0.319507 |
| 7 | 1.765244 | -3.341971 | 1.047376 |
| 7 | 2.060803 | -2.611874 | 2.137802 |
| 6 | 1.540617 | -1.375205 | 2.057420 |
| 7 | 0.877329 | -1.300910 | 0.902014 |
| 6 | 1.755290 | -0.267180 | 2.998239 |
| 6 | 0.678487 | 0.306326 | 3.694828 |
| 6 | 0.918242 | 1.438985 | 4.476516 |
| 6 | 2.197320 | 1.979447 | 4.579299 |
| 6 | 3.263259 | 1.389295 | 3.905949 |
| 6 | 3.042343 | 0.269963 | 3.111340 |
| 1 | 3.863496 | -0.176514 | 2.557756 |
| 1 | 4.263227 | 1.803284 | 3.988054 |
| 1 | 2.361206 | 2.857627 | 5.196528 |
| 1 | 0.094015 | 1.883466 | 5.027048 |
| 6 | -0.678487 | -0.306326 | 3.694828 |
| 6 | -1.755290 | 0.267180 | 2.998239 |
| 6 | -3.042343 | -0.269963 | 3.111340 |
| 6 | -3.263259 | -1.389295 | 3.905949 |
| 1 | -4.263227 | -1.803284 | 3.988054 |
| 6 | -2.197320 | -1.979447 | 4.579299 |
| 1 | -2.361206 | -2.857627 | 5.196528 |
| 6 | -0.918242 | -1.438985 | 4.476516 |

| | | | |
|---|-----------|-----------|-----------|
| 1 | -0.094015 | -1.883466 | 5.027048 |
| 1 | -3.863496 | 0.176514 | 2.557756 |
| 6 | -1.540617 | 1.375205 | 2.057420 |
| 7 | -0.877329 | 1.300910 | 0.902014 |
| 6 | -1.054253 | 2.513218 | 0.319507 |
| 6 | -0.509105 | 2.719270 | -1.015086 |
| 7 | 0.028628 | 1.602541 | -1.550597 |
| 6 | 0.595168 | 1.662665 | -2.758166 |
| 1 | 1.041358 | 0.750665 | -3.138966 |
| 6 | 0.623833 | 2.837003 | -3.499689 |
| 6 | 0.046250 | 3.978608 | -2.956503 |
| 6 | -0.523924 | 3.930256 | -1.689331 |
| 1 | -0.963091 | 4.805091 | -1.223421 |
| 6 | 0.000000 | 5.263969 | -3.747468 |
| 9 | 0.095914 | 6.328157 | -2.943779 |
| 9 | 0.991389 | 5.323358 | -4.641095 |
| 9 | -1.158342 | 5.357921 | -4.412196 |
| 1 | 1.092998 | 2.847635 | -4.476044 |
| 7 | -1.765244 | 3.341971 | 1.047376 |
| 7 | -2.060803 | 2.611874 | 2.137802 |
| 6 | -2.844162 | 3.199040 | 3.209143 |
| 1 | -2.867628 | 2.500883 | 4.044895 |
| 1 | -2.371109 | 4.132950 | 3.514809 |
| 1 | -3.857630 | 3.391630 | 2.853003 |
| 6 | 2.844162 | -3.199040 | 3.209143 |
| 1 | 2.867628 | -2.500883 | 4.044895 |
| 1 | 2.371109 | -4.132950 | 3.514809 |
| 1 | 3.857630 | -3.391630 | 2.853003 |
| 1 | 0.963091 | -4.805091 | -1.223421 |
| 6 | 0.000000 | -5.263969 | -3.747468 |
| 9 | -0.095914 | -6.328157 | -2.943779 |
| 9 | -0.991389 | -5.323358 | -4.641095 |
| 9 | 1.158342 | -5.357921 | -4.412196 |
| 1 | -1.092998 | -2.847635 | -4.476044 |

Table S11. Cartesian coordinates for optimized [Cu(bpye)₂]¹⁺.

| | | | |
|----|-----------|-----------|-----------|
| 29 | -0.000033 | 0.000217 | -0.073690 |
| 7 | -1.352012 | -1.306859 | -0.913615 |
| 6 | -1.102848 | -2.620324 | -1.011647 |
| 1 | -0.077329 | -2.924419 | -0.822442 |
| 6 | -2.077935 | -3.553149 | -1.333605 |
| 6 | -3.373794 | -3.099247 | -1.553667 |
| 1 | -4.169930 | -3.793361 | -1.805806 |

| | | | |
|---|-----------|-----------|-----------|
| 6 | -3.639195 | -1.738023 | -1.447833 |
| 6 | -2.604402 | -0.860604 | -1.130196 |
| 6 | -2.799274 | 0.641026 | -0.997460 |
| 6 | -2.723313 | 1.048521 | 0.467889 |
| 7 | -1.502642 | 0.976885 | 1.031232 |
| 6 | -1.353532 | 1.341236 | 2.311060 |
| 6 | -2.405882 | 1.786366 | 3.099435 |
| 1 | -2.231033 | 2.074864 | 4.130335 |
| 6 | -3.671422 | 1.848878 | 2.527441 |
| 6 | -3.831181 | 1.476600 | 1.196456 |
| 1 | -4.808391 | 1.527644 | 0.730272 |
| 1 | -4.525674 | 2.187804 | 3.105962 |
| 1 | -0.345140 | 1.275784 | 2.710441 |
| 6 | -4.030469 | 1.171543 | -1.722664 |
| 1 | -3.985730 | 0.903799 | -2.782507 |
| 1 | -4.967759 | 0.776847 | -1.317976 |
| 1 | -4.068792 | 2.262477 | -1.648543 |
| 1 | -1.909441 | 1.086677 | -1.466866 |
| 1 | -4.641807 | -1.362671 | -1.617623 |
| 1 | -1.821697 | -4.604458 | -1.408502 |
| 7 | 1.352258 | 1.306814 | -0.913878 |
| 6 | 1.103384 | 2.620316 | -1.012162 |
| 6 | 2.078708 | 3.552874 | -1.334178 |
| 1 | 1.822706 | 4.604223 | -1.409314 |
| 6 | 3.374494 | 3.098652 | -1.554021 |
| 6 | 3.639595 | 1.737392 | -1.447909 |
| 1 | 4.642153 | 1.361798 | -1.617488 |
| 6 | 2.604578 | 0.860253 | -1.130232 |
| 6 | 2.799124 | -0.641390 | -0.997151 |
| 6 | 2.723039 | -1.048492 | 0.468296 |
| 7 | 1.502396 | -0.976298 | 1.031637 |
| 6 | 1.353189 | -1.340272 | 2.311553 |
| 1 | 0.344838 | -1.274317 | 2.710956 |
| 6 | 2.405395 | -1.785609 | 3.100013 |
| 6 | 3.670901 | -1.848701 | 2.528016 |
| 1 | 4.525044 | -2.187802 | 3.106596 |
| 6 | 3.830768 | -1.476771 | 1.196945 |
| 1 | 4.807960 | -1.528214 | 0.730763 |
| 1 | 2.230446 | -2.073834 | 4.130972 |
| 6 | 4.030248 | -1.172316 | -1.722162 |
| 1 | 4.068354 | -2.263240 | -1.647790 |
| 1 | 3.985622 | -0.904797 | -2.782066 |
| 1 | 4.967593 | -0.777714 | -1.317505 |
| 1 | 1.909214 | -1.086961 | -1.466487 |

| | | | |
|---|----------|----------|-----------|
| 1 | 4.170802 | 3.792551 | -1.806205 |
| 1 | 0.077907 | 2.924658 | -0.823124 |

Table S12. Cartesian coordinates for optimized [Cu(bpye)₂]²⁺.

| | | | |
|----|-----------|-----------|-----------|
| 29 | 0.000000 | 0.000000 | 0.391745 |
| 7 | -0.779593 | 1.791462 | -0.175427 |
| 6 | -2.001146 | 2.207862 | 0.186213 |
| 1 | -2.586089 | 1.528898 | 0.794742 |
| 6 | -2.509568 | 3.438648 | -0.196683 |
| 6 | -1.717721 | 4.260254 | -0.987874 |
| 1 | -2.077146 | 5.232241 | -1.310849 |
| 6 | -0.452363 | 3.823708 | -1.367570 |
| 6 | 0.000000 | 2.578636 | -0.946723 |
| 6 | 1.372977 | 2.030733 | -1.313250 |
| 6 | 2.177143 | 1.862299 | -0.037578 |
| 7 | 1.709183 | 0.944519 | 0.828604 |
| 6 | 2.313818 | 0.756928 | 2.012755 |
| 6 | 3.442389 | 1.470895 | 2.381306 |
| 1 | 3.905976 | 1.288711 | 3.343926 |
| 6 | 3.949496 | 2.408367 | 1.488627 |
| 6 | 3.308795 | 2.608950 | 0.270376 |
| 1 | 3.687361 | 3.339969 | -0.433559 |
| 1 | 4.834789 | 2.984706 | 1.738086 |
| 1 | 1.878213 | 0.013214 | 2.673506 |
| 6 | 2.090351 | 2.826394 | -2.395380 |
| 1 | 1.482443 | 2.855763 | -3.303592 |
| 1 | 2.300775 | 3.856533 | -2.092350 |
| 1 | 3.039968 | 2.343734 | -2.642138 |
| 1 | 1.210056 | 1.019248 | -1.715697 |
| 1 | 0.175186 | 4.448650 | -1.990703 |
| 1 | -3.503022 | 3.733878 | 0.120783 |
| 7 | 0.779593 | -1.791462 | -0.175427 |
| 6 | 2.001146 | -2.207862 | 0.186213 |
| 6 | 2.509568 | -3.438648 | -0.196683 |
| 1 | 3.503022 | -3.733878 | 0.120783 |
| 6 | 1.717721 | -4.260254 | -0.987874 |
| 6 | 0.452363 | -3.823708 | -1.367570 |
| 1 | -0.175186 | -4.448650 | -1.990703 |
| 6 | 0.000000 | -2.578636 | -0.946723 |
| 6 | -1.372977 | -2.030733 | -1.313250 |
| 6 | -2.177143 | -1.862299 | -0.037578 |
| 7 | -1.709183 | -0.944519 | 0.828604 |
| 6 | -2.313818 | -0.756928 | 2.012755 |

| | | | |
|---|-----------|-----------|-----------|
| 1 | -1.878213 | -0.013214 | 2.673506 |
| 6 | -3.442389 | -1.470895 | 2.381306 |
| 6 | -3.949496 | -2.408367 | 1.488627 |
| 1 | -4.834789 | -2.984706 | 1.738086 |
| 6 | -3.308795 | -2.608950 | 0.270376 |
| 1 | -3.687361 | -3.339969 | -0.433559 |
| 1 | -3.905976 | -1.288711 | 3.343926 |
| 6 | -2.090351 | -2.826394 | -2.395380 |
| 1 | -3.039968 | -2.343734 | -2.642138 |
| 1 | -1.482443 | -2.855763 | -3.303592 |
| 1 | -2.300775 | -3.856533 | -2.092350 |
| 1 | -1.210056 | -1.019248 | -1.715697 |
| 1 | 2.077146 | -5.232241 | -1.310849 |
| 1 | 2.586089 | -1.528898 | 0.794742 |

Table S13. Cartesian coordinates for optimized $[\text{Cu}(\text{dmby})_2]^{1+}$.

| | | | |
|----|-----------|-----------|-----------|
| 29 | 0.000000 | 0.000000 | 0.008364 |
| 7 | 0.630364 | 1.730298 | 0.935227 |
| 6 | 0.000000 | 2.840929 | 0.506466 |
| 6 | 0.329766 | 4.101559 | 1.003662 |
| 6 | 1.326600 | 4.202721 | 1.965214 |
| 6 | 1.965618 | 3.050758 | 2.404683 |
| 6 | 1.593666 | 1.818222 | 1.866880 |
| 6 | 2.242081 | 0.539995 | 2.299110 |
| 1 | 3.016834 | 0.720053 | 3.048333 |
| 1 | 1.495892 | -0.141849 | 2.722647 |
| 1 | 2.693774 | 0.030118 | 1.440815 |
| 1 | 2.747052 | 3.097117 | 3.155952 |
| 1 | 1.601047 | 5.173345 | 2.366887 |
| 1 | -0.173281 | 4.993689 | 0.651296 |
| 6 | -1.053906 | 2.634009 | -0.518661 |
| 6 | -1.821111 | 3.679668 | -1.031666 |
| 6 | -2.784362 | 3.395878 | -1.990904 |
| 6 | -2.957769 | 2.083876 | -2.411633 |
| 6 | -2.161990 | 1.080325 | -1.858056 |
| 6 | -2.302001 | -0.352977 | -2.266741 |
| 1 | -3.065169 | -0.473327 | -3.039476 |
| 1 | -1.349279 | -0.735698 | -2.649447 |
| 1 | -2.575393 | -0.971881 | -1.404639 |
| 7 | -1.233500 | 1.363982 | -0.930264 |
| 1 | -3.701026 | 1.830425 | -3.160298 |
| 1 | -3.393821 | 4.193294 | -2.404930 |
| 1 | -1.679572 | 4.698793 | -0.693276 |

| | | | |
|---|-----------|-----------|-----------|
| 7 | -0.630364 | -1.730298 | 0.935227 |
| 6 | -1.593666 | -1.818222 | 1.866880 |
| 6 | -1.965618 | -3.050758 | 2.404683 |
| 6 | -1.326600 | -4.202721 | 1.965214 |
| 6 | -0.329766 | -4.101559 | 1.003662 |
| 6 | 0.000000 | -2.840929 | 0.506466 |
| 6 | 1.053906 | -2.634009 | -0.518661 |
| 6 | 1.821111 | -3.679668 | -1.031666 |
| 6 | 2.784362 | -3.395878 | -1.990904 |
| 6 | 2.957769 | -2.083876 | -2.411633 |
| 6 | 2.161990 | -1.080325 | -1.858056 |
| 6 | 2.302001 | 0.352977 | -2.266741 |
| 1 | 3.065169 | 0.473327 | -3.039476 |
| 1 | 1.349279 | 0.735698 | -2.649447 |
| 1 | 2.575393 | 0.971881 | -1.404639 |
| 7 | 1.233500 | -1.363982 | -0.930264 |
| 1 | 3.701026 | -1.830425 | -3.160298 |
| 1 | 3.393821 | -4.193294 | -2.404930 |
| 1 | 1.679572 | -4.698793 | -0.693276 |
| 1 | 0.173281 | -4.993689 | 0.651296 |
| 1 | -1.601047 | -5.173345 | 2.366887 |
| 1 | -2.747052 | -3.097117 | 3.155952 |
| 6 | -2.242081 | -0.539995 | 2.299110 |
| 1 | -3.016834 | -0.720053 | 3.048333 |
| 1 | -1.495892 | 0.141849 | 2.722647 |
| 1 | -2.693774 | -0.030118 | 1.440815 |

Table S14. Cartesian coordinates for optimized $[\text{Cu}(\text{dmby})_2]^{2+}$.

| | | | |
|----|-----------|-----------|-----------|
| 29 | 0.000000 | 0.000000 | 0.005283 |
| 7 | 0.479896 | 1.603449 | 1.109604 |
| 6 | 0.000000 | 2.753704 | 0.585797 |
| 6 | 0.346848 | 3.987160 | 1.122077 |
| 6 | 1.204398 | 4.022465 | 2.215247 |
| 6 | 1.707887 | 2.835614 | 2.725672 |
| 6 | 1.339354 | 1.621154 | 2.145402 |
| 6 | 1.902671 | 0.325357 | 2.636496 |
| 1 | 2.570642 | 0.496846 | 3.482508 |
| 1 | 1.116605 | -0.363631 | 2.958678 |
| 1 | 2.476683 | -0.170543 | 1.846059 |
| 1 | 2.393074 | 2.835194 | 3.565846 |
| 1 | 1.487376 | 4.973614 | 2.654348 |
| 1 | -0.025931 | 4.907640 | 0.691098 |
| 6 | -0.883714 | 2.604635 | -0.588331 |

| | | | |
|---|-----------|-----------|-----------|
| 6 | -1.602699 | 3.659433 | -1.136216 |
| 6 | -2.420925 | 3.411316 | -2.231964 |
| 6 | -2.518499 | 2.121905 | -2.732686 |
| 6 | -1.786305 | 1.092240 | -2.140261 |
| 6 | -1.905653 | -0.319236 | -2.620884 |
| 1 | -2.604685 | -0.377936 | -3.457150 |
| 1 | -0.943119 | -0.717299 | -2.955263 |
| 1 | -2.276867 | -0.971342 | -1.822581 |
| 7 | -0.970544 | 1.357653 | -1.103053 |
| 1 | -3.163676 | 1.897108 | -3.574464 |
| 1 | -2.989211 | 4.219647 | -2.680505 |
| 1 | -1.544620 | 4.654347 | -0.713125 |
| 7 | -0.479896 | -1.603449 | 1.109604 |
| 6 | -1.339354 | -1.621154 | 2.145402 |
| 6 | -1.707887 | -2.835614 | 2.725672 |
| 6 | -1.204398 | -4.022465 | 2.215247 |
| 6 | -0.346848 | -3.987160 | 1.122077 |
| 6 | 0.000000 | -2.753704 | 0.585797 |
| 6 | 0.883714 | -2.604635 | -0.588331 |
| 6 | 1.602699 | -3.659433 | -1.136216 |
| 6 | 2.420925 | -3.411316 | -2.231964 |
| 6 | 2.518499 | -2.121905 | -2.732686 |
| 6 | 1.786305 | -1.092240 | -2.140261 |
| 6 | 1.905653 | 0.319236 | -2.620884 |
| 1 | 2.604685 | 0.377936 | -3.457150 |
| 1 | 0.943119 | 0.717299 | -2.955263 |
| 1 | 2.276867 | 0.971342 | -1.822581 |
| 7 | 0.970544 | -1.357653 | -1.103053 |
| 1 | 3.163676 | -1.897108 | -3.574464 |
| 1 | 2.989211 | -4.219647 | -2.680505 |
| 1 | 1.544620 | -4.654347 | -0.713125 |
| 1 | 0.025931 | -4.907640 | 0.691098 |
| 1 | -1.487376 | -4.973614 | 2.654348 |
| 1 | -2.393074 | -2.835194 | 3.565846 |
| 6 | -1.902671 | -0.325357 | 2.636496 |
| 1 | -2.570642 | -0.496846 | 3.482508 |
| 1 | -1.116605 | 0.363631 | 2.958678 |
| 1 | -2.476683 | 0.170543 | 1.846059 |