# SUPPORTING INFORMATION

## Photoluminescent Cu(I) *vs* Ag(I) complexes: Slowing down emission in Cu(I) complexes by pentacoordinate low-lying excited states

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## FIGURES

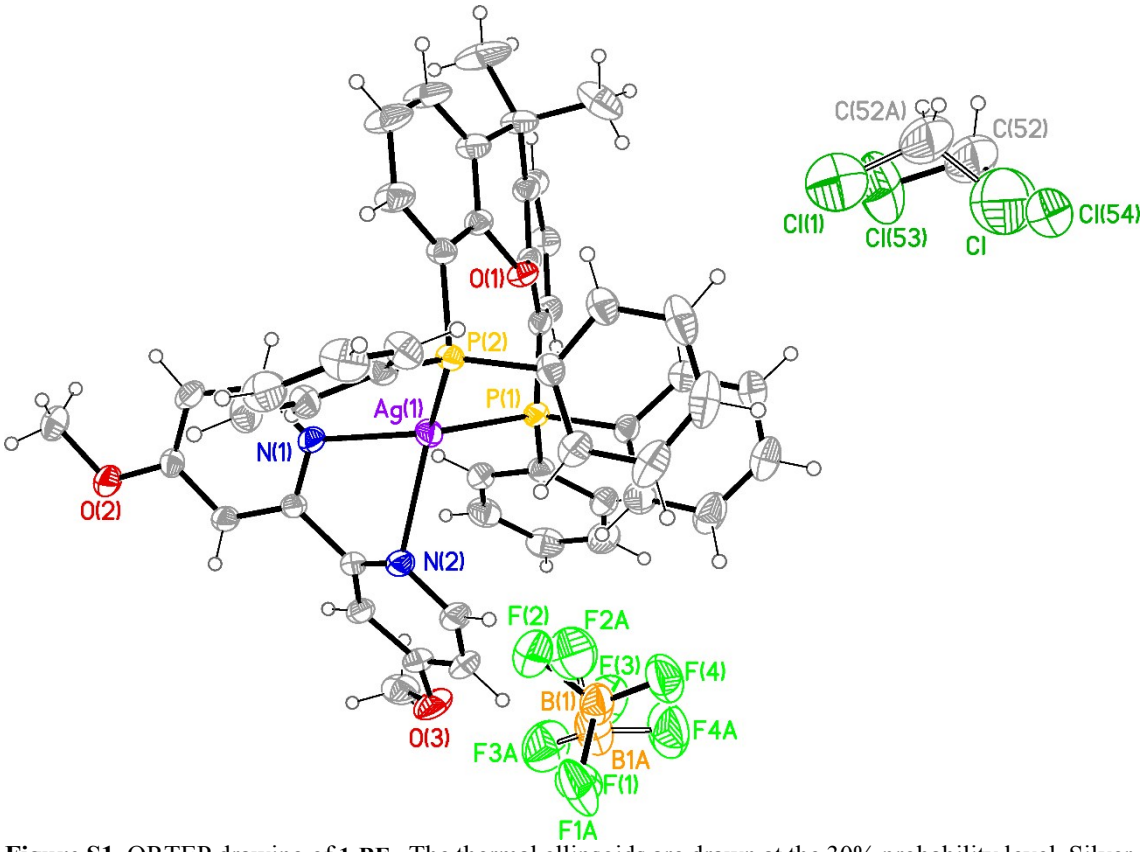



**Figure S1.** ORTEP drawing of **1·BF$_4$**. The thermal ellipsoids are drawn at the 30% probability level. Silver, phosphorous, nitrogen, chorine, fluorine, boron, and carbon atoms are depicted by purple, yellow, blue, dark green, green, brown and grey ellipsoids, respectively. Hydrogens are depicted as grey circles. [The two $BF_4^-$ (B1−F4 and B1A−F4A) and $CH_2Cl_2$ entities (C52, Cl53, Cl54 and Cl, Cl1, C52A), statistically distributed on two positions, are presented).

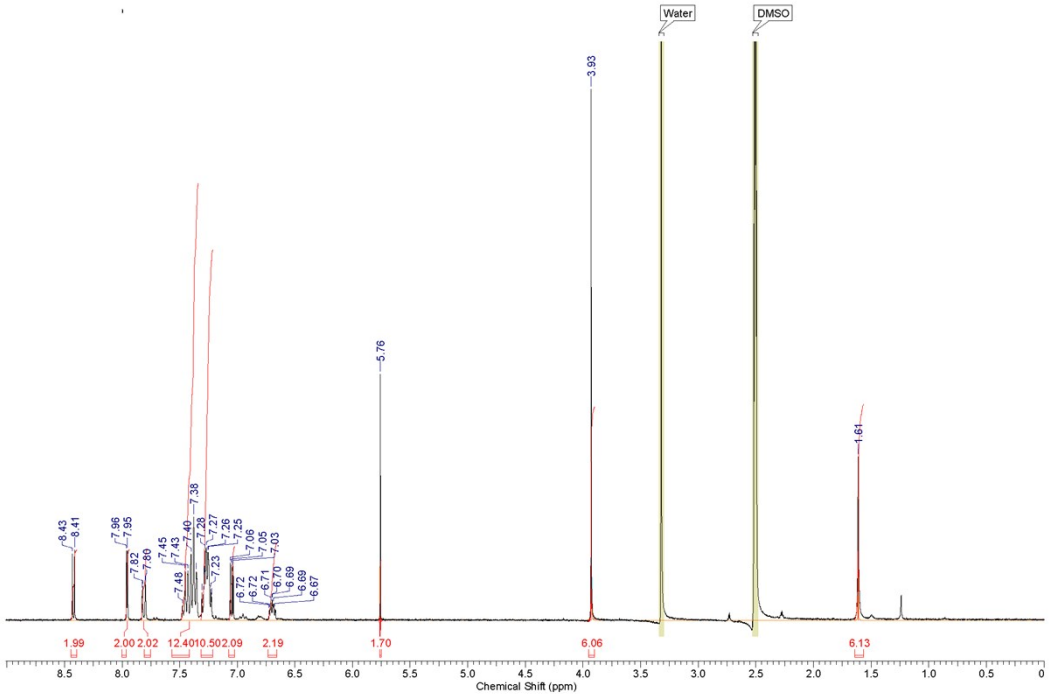



**Fig. S2.** 1H NMR spectrum of **1** in $d_6$-dmso at r.t.

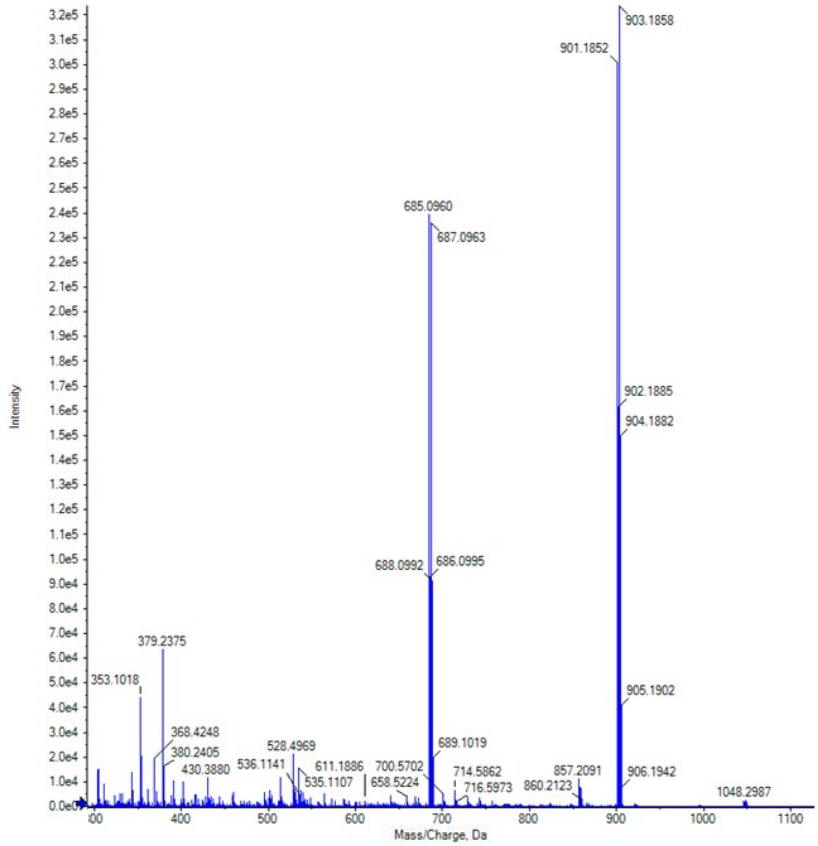



**Fig. S3.** ESI-MS spectrum of **1**.

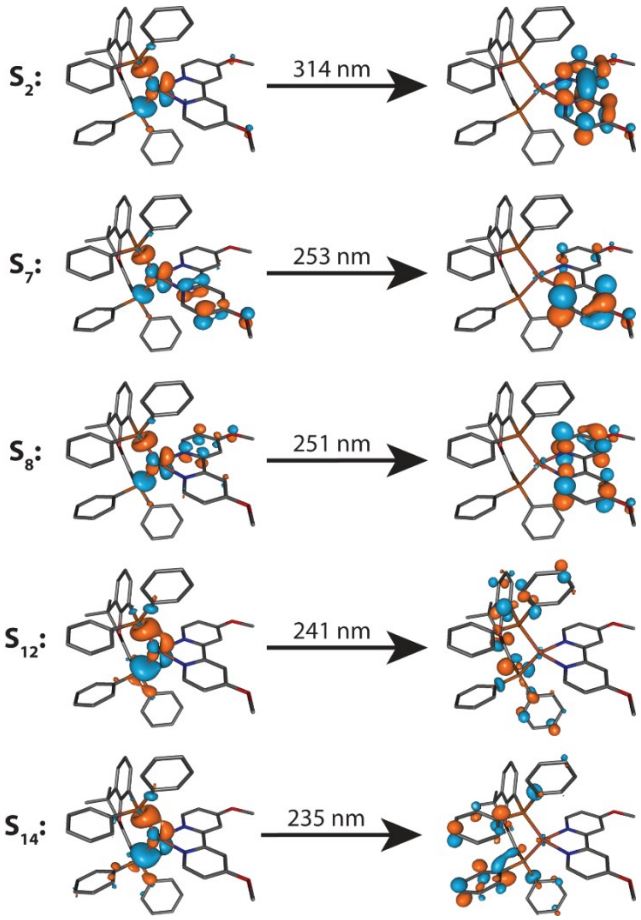



**Figure S4.** Perspective views of the natural transition orbitals (NTOs) involved in the theoretical electronic excitations of **2**. The isodensity surfaces correspond to a cut-off value of 0.05 e bohr$^{-3}$. Electrons are promoted from the orbital at the left side to the other one at the right side. Label $S_i$ indicates the singlet state reached by the $i^{th}$ electronic excitation.

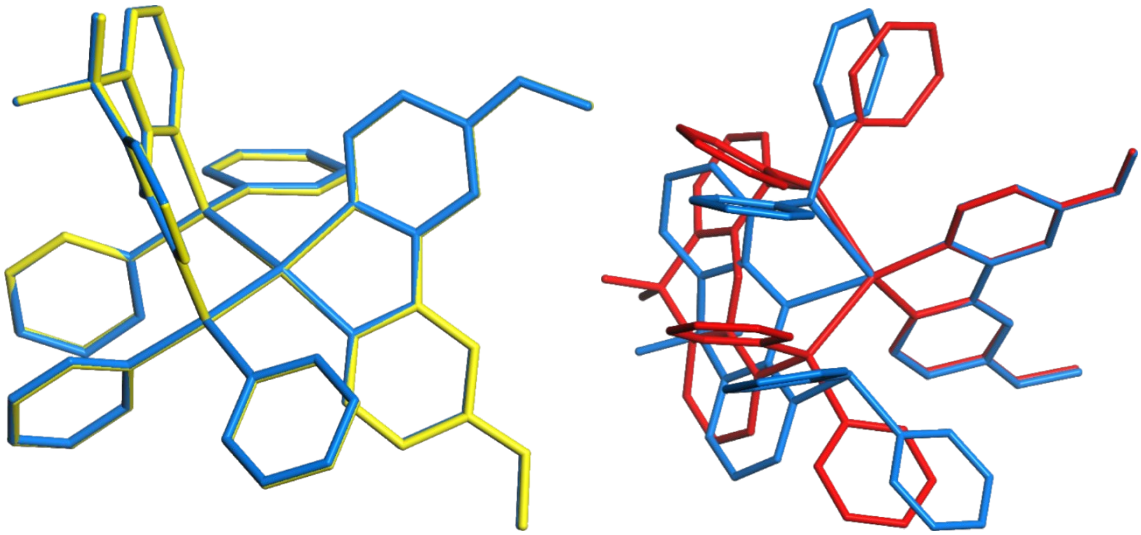


**Figure S5.** View of the optimized geometries of the $S_1$ (blue) and $T_1$ (yellow) states of **2** (left) and the $S_1$ (blue) and $T_1$ (red) states of **2** with the Cu−O bond of the Xantphos ligand (right). The hydrogen atoms are hidden for clarity.

## TABLES

**Table S1.** Crystal data for **1·BF$_4$**.

| | $C_{51}H_{44}AgN_2O_3P_2$, $BF_4 \cdot CH_2Cl_2$ **(1·BF$_4$·DCM)** |
|---|---|
| Formula weight [gmol$^{-1}$] | 1074.43 |
| Crystal system | Triclinic |
| Space group | *P*−1 |
| *a* [Å] | 10.365(4) |
| *b* [Å] | 14.192(6) |
| *c* [Å] | 17.735(6) |
| α [°] | 99.343(19) |
| β [°] | 99.031(19) |
| γ [°] | 98.17(2) |
| V [Å$^3$] | 2504.4(17) |
| Z | 2 |
| $D_{calc}$ [gcm$^{-3}$] | 1.425 |
| μ [mm$^{-1}$] | 0.632 |
| Number of collected reflections (unique) | 34950(9948) |
| Number of observed reflections ($I_o > 2\sigma(I_o)$) | 7260 |
| Internal R factor | 0.048 |
| Number of parameters | 681 |
| Goodness-of-fit S on F$^2$ | 1.033 |
| Largest peak and hole in final difference Fourier map (e Å$^{-3}$) | −0.517 and 0.510 |
| $R_1$[a] [$I > 2.0\sigma(I)$] | 0.0444 (0.714) |
| $wR_2$[b] [all data] | 0.0999 (0.1117) |
| T [K] | 296 |

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$

**Table S2.** Selected bond lengths (Å) and angles (º) for optimized and experimental geometries of the $S_0$ ground state of the [M(Xantphos)(4,4'-$(MeO)_2$-2,2'-bipy)]$BF_4$ [M = Ag (**1·BF$_4$**) and Cu (**2·BF$_4$**)].

| **Compound** | **1·BF$_4$** | **2** | **Optimized 1** |
|---|---|---|---|
| Bond lengths | | | |
| M1−P1 | 2.5461(12) | 2.2460(10) | 2.625 |
| M1−P2 | 2.4407(11) | 2.2513(10) | 2.620 |
| M1−N1 | 2.345(3) | 2.073(3) | 2.375 |
| M1−N2 | 2.423(3) | 2.023(3) | 2.375 |
| M1···O1 | 3.250(1) | 3.198(2) | |
| P1···P2 | 4.097 | 3.843 | |
| Bond angles | | | |
| P1−M1−P2 | 110.48(4) | 117.42(4) | 107.2 |
| N1−M1−N2 | 70.43(9) | 79.82(12) | 70.7 |
| N1−M1−P1 | 114.14(7) | 116.31(9) | 119.7 |
| N1−M1−P2 | 122.07(6) | 109.86(9) | 120.5 |
| P1−M1−N2 | 98.32(7) | 112.83(9) | 117.4 |
| P2−M1−N2 | 135.68(7) | 114.93(9) | 118.1 |

**Table S2.** C–H···X (X = F, Cl) interactions details (distances [Å] and angles[º]) for compounds **1**·$BF_4$.

| Donor–H···Acceptor | D–H | H···A | D···A | D–H···A |
|---|---|---|---|---|
| Compound **1·BF$_4$** | | | | |
| C24–H24···F4 | 0.93 | 2.553(1) | 3.209(1) | 127.86(4) |
| C46–H46···F1 | 0.93 | 2.492(1) | 3.418(1) | 173.40(6) |
| C49–H49···F2 | 0.93 | 2.427(1) | 3.298(1) | 156.01(5) |
| C49–H49···F3 | 0.93 | 2.497(1) | 3.2311) | 135.98(5) |
| C24–H24···F4A | 0.93 | 2.461(1) | 3.334(1) | 156.05(6) |
| C46–H46···F1A | 0.93 | 2.360(1) | 3.230(1) | 172.20(6) |
| C49–H49···F2A | 0.93 | 2.566(1) | 3.483(1) | 168.82(6) |
| C49–H49···F3A | 0.93 | 2.462(1) | 3.036(1) | 120.07(5) |
| C37–H37···Cl1 | 0.93 | 3.20 | 3.788(1) | 128.03(7) |
| C51–H51B···Cl54 | 0.96 | 2.920(1)(1) | 3.390(1) | 111.40(4) |
| C52-H52A···F3 | 0.96 | 2.700(1) | 3.639(1) | 163.04(4) |
| C52-H52A···F3A | 0.96 | 2.549(1) | 3.210(1)A | 111.04(3) |

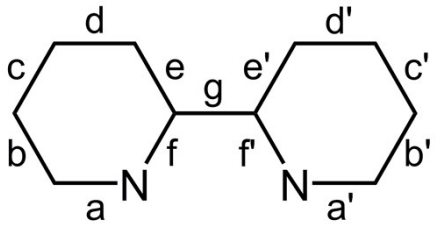
**Table S3.** Dihedral angle ($\theta$, in degrees) between $MN_2$ and $MP_2$ planes for the optimized geometries of **1** and **2** using a solvation model. The values in parentheses correspond to those obtained from the experimental geometries of **1·BF$_4$** and **2·BF$_4$**.

| **Geometry** | **$S_0$** | **$S_1$** | **$T_1$** | **Ox** | **$S_1$'** | **$T_1$'** | **Ox'** |
|---|---|---|---|---|---|---|---|
| **1** | 90.0 (75.9) | 43.1 | 45.4 | 47.7 | | | |
| **2 ae** [a] | 89.9 (86.4) | 57.3 | 58.4 | 57.9 | | | |
| **2 ae (Cu−O)** [a, b] | | | | | 80.1 | 80.0 | 89.5 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **2 p** [a] | 89.8 (86.4) | 55.8 | 57.3 | 57.6 | | | |
| **2 p (Cu−O)** [a, b] | | | | | 69.7 | 77.9 | 85.9 |

[a] Set basis all electron (ae) and pseudo (p). [b] optimized geometry of **2** with an additional Cu−O bond of the Xantphos ligand.

**Table S4.** Bond lengths of compounds **1** and **2** at the optimized geometries.




| Model | | $S_0$ [a] | Ox [a] | $S_1$ [a] | $T_1$ [a] |
|---|---|---|---|---|---|
| **1** | a | 1.351 | 1.352 | 1.356 | 1.354 |
| | b | 1.387 | 1.384 | 1.376 | 1.378 |
| | c | 1.404 | 1.405 | 1.429 | 1.427 |
| | d | 1.400 | 1.403 | 1.379 | 1.379 |
| | e | 1.402 | 1.397 | 1.433 | 1.434 |
| | f | 1.350 | 1.355 | 1.388 | 1.394 |
| | g | 1.494 | 1.487 | 1.422 | 1.418 |
| | a’ | 1.344 | 1.345 | 1.352 | 1.350 |
| | b’ | 1.395 | 1.392 | 1.381 | 1.384 |
| | c’ | 1.400 | 1.402 | 1.427 | 1.425 |
| | d’ | 1.403 | 1.406 | 1.380 | 1.381 |
| | e’ | 1.394 | 1.389 | 1.426 | 1.428 |
| | f’ | 1.358 | 1.362 | 1.392 | 1.397 |
| **2ae** | a | 1.351 | 1.346 | 1.352 | 1.359 |
| | b | 1.386 | 1.390 | 1.380 | 1.376 |
| | c | 1.405 | 1.404 | 1.427 | 1.430 |
| | d | 1.401 | 1.408 | 1.382 | 1.379 |
| | e | 1.399 | 1.383 | 1.421 | 1.430 |
| | f | 1.353 | 1.365 | 1.390 | 1.397 |
| | g | 1.488 | 1.479 | 1.422 | 1.416 |
| | a’ | 1.344 | 1.354 | 1.361 | 1.350 |
| | b’ | 1.394 | 1.383 | 1.373 | 1.383 |
| | c’ | 1.401 | 1.407 | 1.430 | 1.425 |
| | d’ | 1.404 | 1.405 | 1.379 | 1.383 |
| | e’ | 1.391 | 1.391 | 1.429 | 1.422 |
| | f’ | 1.361 | 1.359 | 1.390 | 1.396 |
| **2p** | a | 1.352 | 1.346 | 1.353 | 1.360 |
| | b | 1.386 | 1.390 | 1.380 | 1.376 |
| | c | 1.405 | 1.404 | 1.427 | 1.430 |
| | d | 1.401 | 1.408 | 1.382 | 1.379 |
| | e | 1.399 | 1.384 | 1.421 | 1.430 |
| | f | 1.353 | 1.364 | 1.390 | 1.397 |
| | g | 1.489 | 1.481 | 1.423 | 1.417 |
| | a’ | 1.345 | 1.354 | 1.362 | 1.351 |
| | b’ | 1.394 | 1.383 | 1.373 | 1.382 |
| | c’ | 1.401 | 1.407 | 1.430 | 1.426 |
| | d’ | 1.404 | 1.405 | 1.379 | 1.383 |
| | e’ | 1.391 | 1.392 | 1.429 | 1.423 |
| | f’ | 1.361 | 1.359 | 1.389 | 1.396 |

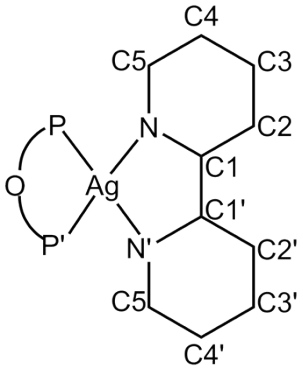
[a] ae = all electron basis set; p = pseudo basis set.

**Table S5.** A selection of experimental and theoretical electronic transitions in the UV-Vis region of **1**. Results appears as wavelengths ($\lambda$) in nm and oscillator strengths ($f$), respectively.

| Compound | $\lambda$ (solv)[a,b] | $\lambda_{exp}$ [c] | Nature |
|---|---|---|---|
| **1** | [2] 270.4 (0.131) | 280 | MLCT (bipy) |
| | [3] 250.0 (0.156) | 250 | MLCT (bipy) |
| | [11] 233.5 (0.265) | < 240 | MLCT (bipy + Xantphos) |
| | [17] 224.7 (0.203) | | MLCT (Xantphos) |
| | [20] 222.8 (0.200) | | MLCT (Xantphos) |
| | [21] 219.6 (0.314) | | MLCT (Xantphos) |
| | [23] 209.3 (0.317) | | π−π* (bipy) |
| **2ae** | [2] 324.5 (0.144) | 372 | MLCT (bipy) |
| | [9] 252.4 (0.148) | | π−π* + MLCT (bipy) |
| | [11] 243.5 (0.127) | 285 | π−π* + MLCT (bipy) |
| | [12] 241.9 (0.072) | | MLCT (Xantphos) |
| | [15] 237.0 (0.155) | | MLCT (Xantphos) |
| | [16] 235.7 (0.111) | | MLCT (Xantphos) |
| **2p** | [2] 314.4 (0.144) | 372 | MLCT (bipy) |
| | [7] 253.3 (0.083) | | π−π* + MLCT (bipy) |
| | [8] 251.1 (0.119) | 285 | π−π* + MLCT (bipy) |
| | [12] 240.8 (0.190) | | MLCT (Xantphos) |
| | [14] 235.2 (0.137) | | MLCT (Xantphos) |
| | [20] 280.1 (0.112) | | MLCT (Xantphos) |

[a] Number of the electronic excitation (bracket), wavelength (in nm), and oscillator strength ($f$ x $10^4$, parentheses). [b] Geometries optimized and TDDFT using a solvation model. [c] Wavelengths (in nm) found from a deconvolution of the experimental spectra.

**Table S6.** Atomic charges obtained by NBO analysis of compound **1** at the optimized gas geometries.



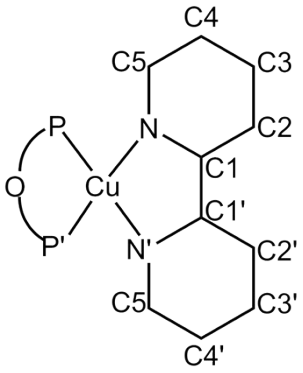

| Charges /Atom | $S_0$ | $S_1$ | $T_1$ | Ox |
|---|---|---|---|---|
| Ag | 0.546 | 0.8222 | 0.805 | 0.819 |
| P | 0.783 | 0.841 | 0.849 | 0.899 |
| P’ | 0.782 | 0.835 | 0.849 | 0.911 |
| N | −0.550 | −0.553 | −0.554 | −0.555 |
| N’ | −0.559 | −0.591 | −0.585 | −0.573 |
| C1 | −0.556 | −0.591 | −0.588 | −0.567 |
| C1’ | 0.205 | 0.148 | 0.136 | 0.211 |
| C2 | 0.221 | 0.147 | 0.141 | 0.229 |
| C2’ | −0.259 | −0.300 | −0.303 | −0.248 |
| C3 | −0.306 | −0.343 | −0.345 | −0.297 |
| C3’ | 0.369 | 0.344 | 0.348 | 0.387 |
| C4 | 0.369 | 0.344 | 0.346 | 0.387 |
| C4’ | −0.326 | −0.377 | −0.384 | −0.317 |
| C5 | −0.279 | −0.341 | −0.347 | −0.270 |
| C5’ | 0.089 | 0.082 | 0.084 | 0.103 |

**Table S7.** Atomic spin densities obtained by NBO analysis of compound **1** at the optimized gas geometries.




| Charges /Atom | $S_0$ | $T_1$ | Ox |
|---|---|---|---|
| Ag | 0 | 0.331 | 0.273 |
| P | 0 | 0.106 | 0.209 |
| P’ | 0 | 0.115 | 0.216 |
| N | 0 | 0.000 | 0.000 |
| N’ | 0 | 0.352 | 0.090 |
| C1 | 0 | 0.361 | 0.094 |
| C1’ | 0 | 0.130 | −0.004 |
| C2 | 0 | 0.151 | −0.004 |
| C2’ | 0 | 0.114 | 0.004 |
| C3 | 0 | 0.093 | 0.004 |
| C3’ | 0 | 0.009 | −0.003 |
| C4 | 0 | 0.013 | −0.003 |
| C4’ | 0 | 0.156 | 0.005 |
| C5 | 0 | 0.170 | 0.006 |
| C5’ | 0 | −0.080 | −0.008 |

**Table S8.** Atomic charges obtained by NBO analysis of compound **2** with all electron basis set at the optimized geometries.




| **Charges /Atom** | **$S_0$** | **$S_1$** | **$T_1$** | **Ox** | **$S_1$'** | **$T_1$'** | **Ox'** |
|---|---|---|---|---|---|---|---|
| Cu | 0.808 | 1.158 | 1.192 | 1.179 | 1.218 | 1.258 | 1.430 |
| P | 0.724 | 0.752 | 0.750 | 0.775 | 0.717 | 0.710 | 0.692 |
| P’ | 0.724 | 0.754 | 0.754 | 0.775 | 0.741 | 0.743 | 0.694 |
| O | −0.559 | −0.562 | −0.562 | −0.563 | −0.563 | −0.560 | −0.524 |
| N | −0.616 | −0.668 | −0.676 | −0.630 | −0.640 | −0.647 | −0.674 |
| N’ | −0.623 | −0.683 | −0.693 | −0.639 | −0.696 | −0.708 | −0.687 |
| C1 | 0.203 | 0.147 | 0.143 | 0.214 | 0.138 | 0.138 | 0.217 |
| C1’ | 0.217 | 0.148 | 0.143 | 0.233 | 0.145 | 0.142 | 0.237 |
| C2 | −0.257 | −0.299 | −0.304 | −0.242 | −0.291 | −0.301 | −0.246 |
| C2’ | −0.304 | −0.340 | −0.344 | −0.290 | −0.337 | −0.345 | −0.294 |
| C3 | 0.371 | 0.347 | 0.353 | 0.399 | 0.336 | 0.349 | 0.405 |
| C3’ | 0.371 | 0.344 | 0.347 | 0.399 | 0.337 | 0.347 | 0.407 |
| C4 | −0.326 | −0.374 | −0.384 | −0.315 | −0.362 | −0.382 | −0.307 |
| C4’ | −0.279 | −0.333 | −0.345 | −0.267 | −0.327 | −0.348 | −0.259 |
| C5 | 0.0940 | 0.086 | 0.089 | 0.111 | 0.071 | 0.083 | 0.113 |
| C5’ | 0.078 | 0.067 | 0.070 | 0.093 | 0.065 | 0.077 | 0.095 |

**Table S9.** Atomic spin densities obtained by NBO analysis of compound **2** with all electron basis set at the optimized geometries.




| Charges /Atom | $S_0$ | $S_1$ | $T_1$ | Ox | $S_1$' | $T_1$' | Ox' |
|---|---|---|---|---|---|---|---|
| Cu | 0 | 0 | 0.545 | 0.531 | 0 | 0.588 | 0.850 |
| P | 0 | 0 | 0.064 | 0.107 | 0 | 0.003 | −0.003 |
| P’ | 0 | 0 | 0.070 | 0.107 | 0 | 0.072 | −0.003 |
| O | 0 | 0 | 0.000 | 0.000 | 0 | 0.008 | 0.014 |
| N | 0 | 0 | 0.291 | 0.106 | 0 | 0.352 | 0.040 |
| N’ | 0 | 0 | 0.316 | 0.105 | 0 | 0.268 | 0.040 |
| C1 | 0 | 0 | 0.121 | −0.004 | 0 | 0.130 | 0.006 |
| C1’ | 0 | 0 | 0.167 | −0.005 | 0 | 0.152 | 0.008 |
| C2 | 0 | 0 | 0.107 | 0.003 | 0 | 0.102 | −0.007 |
| C2’ | 0 | 0 | 0.075 | 0.004 | 0 | 0.084 | −0.007 |
| C3 | 0 | 0 | 0.014 | −0.002 | 0 | 0.017 | 0.012 |
| C3’ | 0 | 0 | 0.031 | −0.003 | 0 | 0.021 | 0.012 |
| C4 | 0 | 0 | 0.145 | 0.005 | 0 | 0.144 | 0.024 |
| C4’ | 0 | 0 | 0.153 | 0.005 | 0 | 0.160 | 0.026 |
| C5 | 0 | 0 | −0.070 | −0.007 | 0 | −0.074 | −0.014 |
| C5’ | 0 | 0 | −0.070 | −0.006 | 0 | −0.074 | −0.016 |

**Table S10.** Atomic charges obtained by NBO analysis of compound **2** with pseudo basis set at the optimized geometries.




| Charges /Atom | $S_0$ | $S_1$ | Ox | $T_1$ | $S_1$' | $T_1$' | Ox' |
|---|---|---|---|---|---|---|---|
| Cu | 0.373 | 0.810 | 0.822 | 0.799 | 0.792 | 0.749 | 0.725 |
| P | 0.832 | 0.839 | 0.871 | 0.850 | 0.825 | 0.834 | 0.859 |
| P’ | 0.831 | 0.841 | 0.865 | 0.850 | 0.849 | 0.866 | 0.882 |
| N | −0.550 | −0.554 | −0.555 | −0.555 | −0.561 | −0.560 | −0.531 |
| N’ | −0.554 | −0.620 | −0.585 | −0.622 | −0.605 | −0.588 | −0.534 |
| C1 | −0.558 | −0.632 | −0.590 | −0.636 | −0.635 | −0.630 | −0.573 |
| C1’ | 0.207 | 0.150 | 0.216 | 0.147 | 0.152 | 0.143 | 0.219 |
| C2 | 0.222 | 0.152 | 0.236 | 0.148 | 0.151 | 0.148 | 0.229 |
| C2’ | −0.256 | −0.296 | −0.241 | −0.301 | −0.295 | −0.299 | −0.240 |
| C3 | −0.302 | −0.336 | −0.289 | −0.340 | −0.337 | −0.343 | −0.289 |
| C3’ | 0.372 | 0.347 | 0.398 | 0.353 | 0.346 | 0.349 | 0.398 |
| C4 | 0.372 | 0.343 | 0.398 | 0.348 | 0.343 | 0.348 | 0.3917 |
| C4’ | −0.323 | −0.369 | −0.313 | −0.380 | −0.368 | −0.378 | −0.311 |
| C5 | −0.277 | −0.329 | −0.266 | −0.342 | −0.329 | −0.344 | −0.266 |
| C5’ | 0.096 | 0.088 | 0.114 | 0.092 | 0.089 | 0.087 | 0.109 |

**Table S11.** Atomic spin densities obtained by NBO analysis of compound **2** with pseudo basis set at the optimized gas geometries.




| Charges /Atom | $S_0$ | $S_1$ | $T_1$ | Ox | $S_1$' | $T_1$' | Ox' |
|---|---|---|---|---|---|---|---|
| Cu | 0 | 0 | 0.542 | 0.511 | 0 | 0.574 | 0.570 |
| P | 0 | 0 | 0.070 | 0.119 | 0 | 0.006 | 0.0468 |
| P’ | 0 | 0 | 0.074 | 0.115 | 0 | 0.083 | 0.094 |
| N | 0 | 0 | 0.000 | 0.000 | 0 | 0.008 | −0.003 |
| N’ | 0 | 0 | 0.286 | 0.102 | 0 | 0.345 | 0.182 |
| C1 | 0 | 0 | 0.309 | 0.098 | 0 | 0.270 | 0.045 |
| C1’ | 0 | 0 | 0.123 | −0.004 | 0 | 0.133 | −0.011 |
| C2 | 0 | 0 | 0.169 | −0.004 | 0 | 0.153 | 0.000 |
| C2’ | 0 | 0 | 0.103 | 0.004 | 0 | 0.099 | 0.009 |
| C3 | 0 | 0 | 0.071 | 0.004 | 0 | 0.082 | 0.000 |
| C3’ | 0 | 0 | 0.018 | −0.002 | 0 | 0.019 | −0.008 |
| C4 | 0 | 0 | 0.035 | −0.003 | 0 | 0.022 | −0.002 |
| C4’ | 0 | 0 | 0.139 | 0.005 | 0 | 0.140 | 0.011 |
| C5 | 0 | 0 | 0.147 | 0.005 | 0 | 0.157 | 0.002 |
| C5’ | 0 | 0 | −0.066 | −0.006 | 0 | −0.071 | −0.015 |

**Table S12.** Zero-point energies (in eV) and free energies at 298 K (in eV) of the different states of **1** and **2** with all electron basis set (ae) and with pseudo basis set (p) in the optimized geometry.

| Compound | $S_0$ | $T_1$ | Ox | $T_1$' | Ox' |
|---|---|---|---|---|---|
| **Zero-point energies** | | | | | |
| **1** | 0 | 2.76 | 5.97 | | |
| **2 ae** | 0 | 2.15 | 5.49 | 2.11 | 7.04 |
| **2 p** | 0 | 2.31 | 5.67 | 2.27 | 5.61 |
| **Free energies** | | | | | |
| **1** | 0 | 2.87 | 6.09 | | |
| **2 ae** | 0 | 2.21 | 5.59 | 2.09 | 7.09 |
| **2 p** | 0 | 2.39 | 5.80 | 2.31 | 5.70 |