Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis of Copper(I) Cyclic (Alkyl)(Amino)Carbene Complexes with Potentially Bidentate N^N, N^S and S^S Ligands for Efficient White Photoluminescence

Alexander S. Romanov, Florian Chotard, Jahan Rashid, and Manfred Bochmann *
School of Chemistry, University of East Anglia, Earlham Road, Norwich, NR4 7TJ, UK

SUPPORTING INOFORMATION

X-Ray Crystallography. Crystals of **3** suitable for X-ray diffraction study were obtained by layering a CH_2Cl_2 solution with hexane. The atoms C3, C17, C18, C19 and C20 were disordered over two positions with occupancies 0.45/0.55 for complex **3** with SADI restraint. Crystals of **4** and **5** were obtained by slow evaporation of Et_2O solution under argon atmosphere. The atoms C2, C3, C4, C17, C18, C19, C20, C40, C41 and C42 were disordered over two half-populated positions for complex **5** with SADI restraint. Crystals were mounted in oil on glass fiber and fixed on the diffractometer in a cold nitrogen stream. Data were collected using an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer with graphite monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) at 140 K. Data were processed using the CrystAlisPro-CCD and –RED software.[1] The structure was solved by direct methods and refined by the full-matrix least-squares against F^2 in an anisotropic (for non-hydrogen atoms) approximation. All hydrogen atom positions were refined in isotropic approximation in a "riding" model with the $U_{iso}(H)$ parameters equal to 1.2 $U_{eq}(C_i)$, for methyl groups equal to 1.5 $U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are respectively the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded. All calculations were performed using the SHELXTL software.[2]

The principal crystallographic data for complex **3**: CCDC number 1915487, $C_{33}H_{39}CuN_2S_2$, Monoclinic, space group $P2_1/c$, $a = 15.6402(4)$ Å, $b = 10.5052(3)$ Å, $c = 18.5040(4)$ Å, $\beta = 95.757(2)°$, $V = 3024.94(13)$ Å^3, $Z = 4$, $d_{calc} = 1.298$ g cm^{-3}, $\mu = 0.884$ mm^{-1}, red/plate, crystal size 0.46 × 0.35 × 0.13 mm, $F(000) = 1248.0$, T_{min}/T_{max} 0.86995/1.00000, 27770 reflections measured ($5.884° \leq 2\Theta \leq 55.996°$), 7286 unique ($R_{int} = 0.0283$, $R_{sigma} = 0.0275$)

which were used in all calculations. The final R_1 was 0.0351 (I > 2σ(I)) and wR_2 was 0.0875 (all data), *GOF* = 1.046, $\Delta\rho_{min}/\Delta\rho_{max}$ = 0.63/–0.67.

The principal crystallographic data for complex **4**: CCDC number 1915489, $C_{47}H_{71}CuN_4$, Monoclinic, space group *P2₁/n*, *a* = 14.3631(4) Å, *b* = 17.2867(4) Å, *c* = 18.3895(5) Å, β = 102.166(3)°, *V* = 4463.4(2) Å^3, *Z* = 4, d_{calc} = 1.124 g cm^{-3}, μ = 0.524 mm^{-1}, yellow/block, crystal size 0.38 × 0.23 × 0.16 mm, *F*(000) = 1640.0, T_{min}/T_{max} 0.89063/1.00000, 45078 reflections measured (6.208 ° ≤ 2Θ ≤ 56.000°), 10763 unique (R_{int} = 0.0358, R_{sigma} = 0.0324) which were used in all calculations. The final R_1 was 0.0354 (I > 2σ(I)) and wR_2 was 0.0963 (all data), *GOF* = 1.004, $\Delta\rho_{min}/\Delta\rho_{max}$ = 0.40/–0.29.

The principal crystallographic data for complex **5**: CCDC number 1915488, $C_{45}H_{66}CuN_3$, Triclinic, space group *P-1*, *a* = 11.8424(2) Å, *b* = 13.8008(4) Å, *c* = 15.1018(4) Å, α = 110.681(2)°, β = 93.732(2)°, γ = 111.814(2)°, *V* = 2088.29(10) Å^3, *Z* = 2, d_{calc} = 1.133 g cm^{-3}, μ = 0.555 mm^{-1}, colourless/block, crystal size 0.37 × 0.29 × 0.23 mm, *F*(000) = 772.0, T_{min}/T_{max} 0.92522/1.00000, 20795 reflections measured (5.92 ° ≤ 2Θ ≤ 55.998°), 10073 unique (R_{int} = 0.0280, R_{sigma} = 0.0453) which were used in all calculations. The final R_1 was 0.0424 (I > 2σ(I)) and wR_2 was 0.1054 (all data), *GOF* = 1.035, $\Delta\rho_{min}/\Delta\rho_{max}$ = 0.87/–0.50.

Table S1. UV/vis absorption data in THF solution at 298 K.

Complex	UV/vis deaerated THF nm (10^3 ε/M^{-1} cm^{-1}),
1	282 (15.1), 331 (23.4)
2	272 (8.5), 365 (3.28)
3	286 (17.1), 362 (19.3)
4	250 (14.3), 285 (5.74)
5	272 (14.3), 359 (3.11)
6	266 (16.6), 327 (16.1)

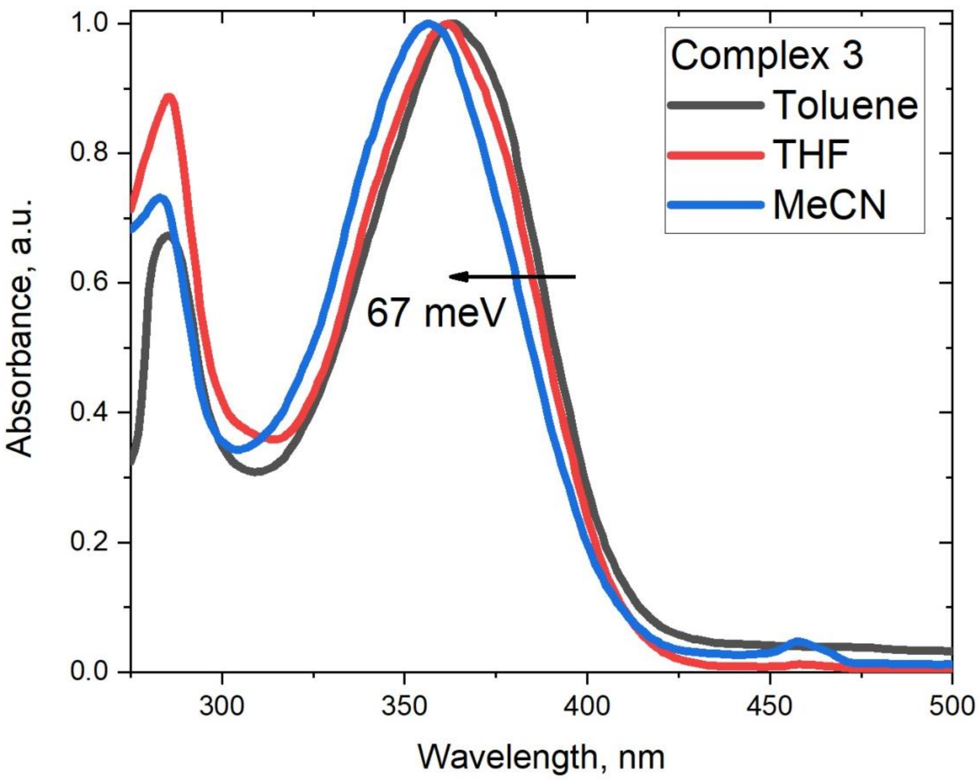

Figure S1. UV-Vis spectra for copper complex **3** in different solvents.

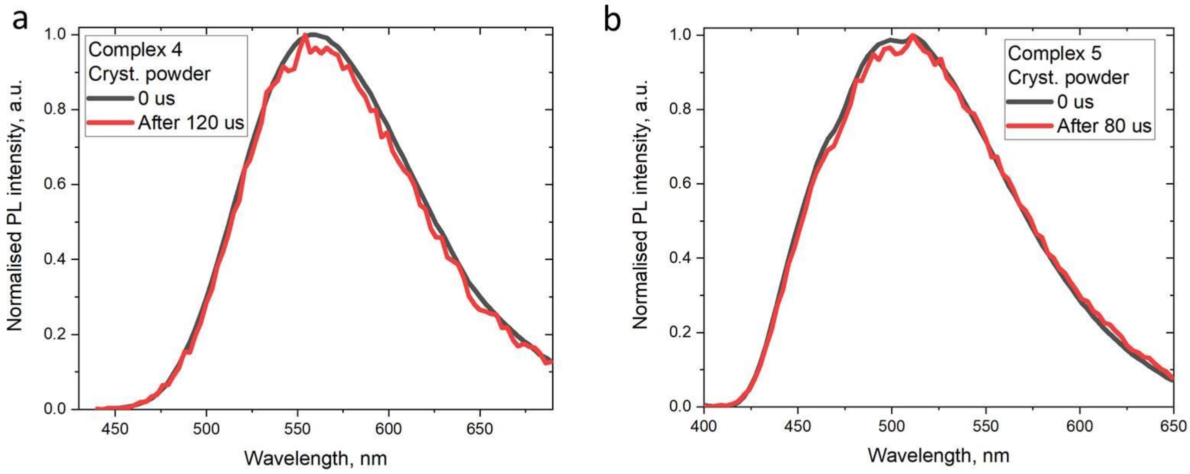

Figure S2. Time-resolved emission spectra for **$^{\mathrm{Me2}}\mathrm{LCuN_2CNMe_2}$ (4)** and **$^{\mathrm{Me2}}\mathrm{LCuN_2CH}$ (5)** Excited at 380 nm at 298K.

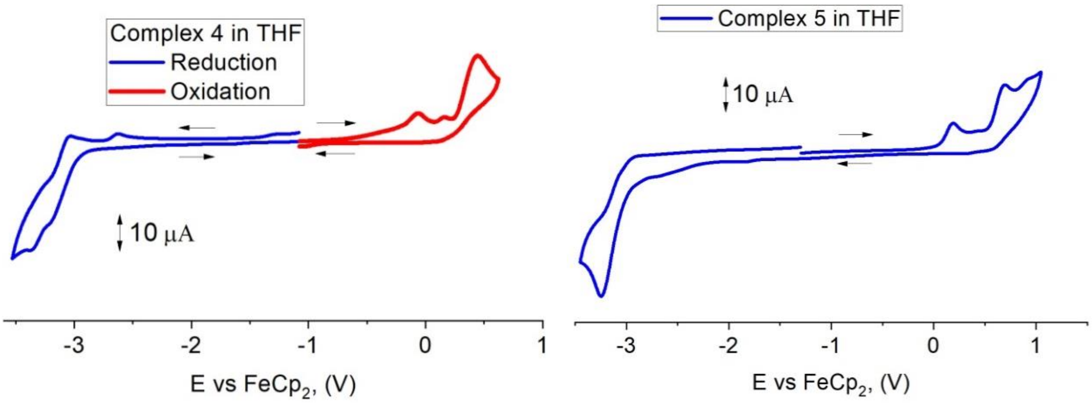

Figure S3. Full range cyclic voltammograms for ($^{\mathrm{Me}}$L)Cu(Guanidinate) (**4**, left) and ($^{\mathrm{Me}}$L)Cu(Formamidinate) (**5**, right), recorded using a glassy carbon electrode in THF solution (1.4 mM) with [n-Bu$_4$N]PF$_6$ as supporting electrolyte (0.13 M), scan rate 0.1 Vs^{-1}.

---

[1] *Programs CrysAlisPro*, Oxford Diffraction Ltd., Abingdon, UK (2010).

[2] a. Sheldrick, G.M. SHELX-97 and SHELXL – Programs for crystal structure determination (SHELXS) and refinement (SHELXL), *Acta Cryst.* **2008**, *A64*, 112.
b. G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access).