Electronic Supplementary Information

# Highly efficient cuprous complexes with thermally activated delayed fluorescence and simplified solution process OLEDs using the ligand as host

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Detailed derivations of eq. 4 and eq. 5:

**eq.4**

$$\frac{I(T_1)}{I_{tot}} = \frac{I(T_1)}{I(S_1)+I(T_1)} = \left[1+\frac{I(S_1)}{I(T_1)}\right]^{-1} = \left[1+\frac{\alpha N(S_1)\Phi_{PL}(S_1)\tau(S_1)^{-1}}{\alpha N(T_1)\Phi_{PL}(T_1)\tau(T_1)^{-1}}\right]^{-1} =$$

$$\left[1+\frac{N(S_1)\Phi_{PL}(S_1)\tau(T_1)}{N(T_1)\Phi_{PL}(T_1)\tau(S_1)}\right]^{-1}$$

$$= \left[1+\frac{\Phi_{PL}(S_1)\tau(T_1)g(S_1)}{\Phi_{PL}(T_1)\tau(S_1)g(T_1)}\exp\left(-\frac{\Delta E_{ST}}{k_B T}\right)\right]^{-1}$$

**eq. 5**

$$\frac{I(S_1)}{I_{tot}} = 1-\frac{I(T_1)}{I_{tot}} = 1-\left[1+\frac{\Phi_{PL}(S_1)\tau(T_1)g(S_1)}{\Phi_{PL}(T_1)\tau(S_1)g(T_1)}\exp\left(-\frac{\Delta E_{ST}}{k_B T}\right)\right]^{-1}$$

The splitting of the $T_1$ state, that is, the zero-field splitting (ZFS), is distinct in organo-transition-metal compounds due to the high metal participation and large spin-orbit coupling[1]. So, we take into account the degeneracy factors for the singlet and the triplet states ($g(S_1) = 1$ and $g(T_1) = 3$) in evaluating the populations of the two states (Boltzmann distribution).

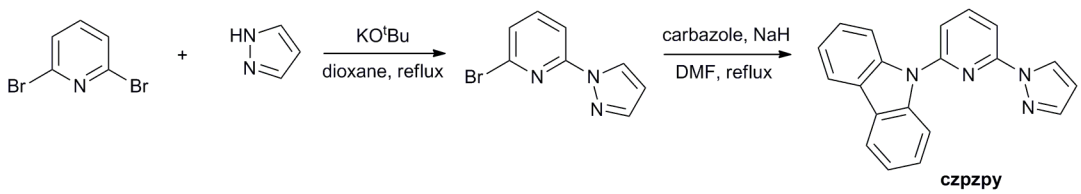


**Fig. S1** Synthesis of czpzpy.

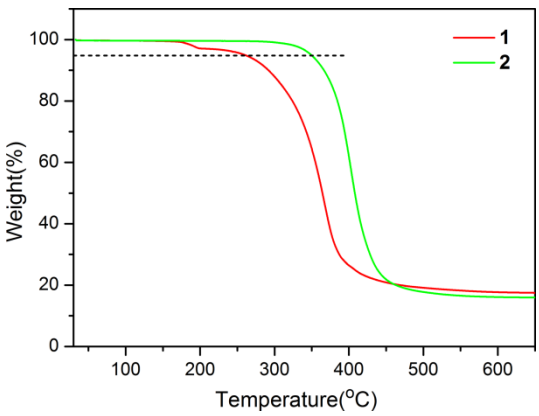


**Fig. S2** TGA-plots for complexes **1** and **2**. The black dashed line marks 95% of the original sample weight.

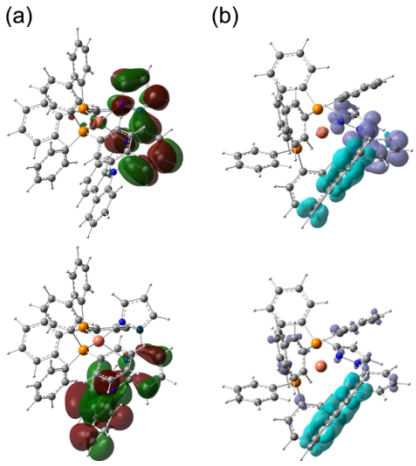


**Fig. S3** (a) The HOMO (lower image) and LUMO (upper image) of ground state of **1**. (b) Redistribution of electron densities of lowest singlet excited state (upper image) and the lowest triplet excited state (lower image) of **1**. The blue area denotes charge density decrease while the purple area denotes charge density increase.

**Table S1.** Photophysical parameters of the complexes in degassed $CH_2Cl_2$ at room temperature

| complex | $\lambda_{exc}$ [nm] | $\lambda_{em}$ [nm] | Stokes shifts |
|---|---|---|---|
| **1** | 381 | 540 | 159 |
| **2** | 386 | 569 | 183 |

**Table S2.** Properties of the first excited singlet and triplet states

| Complex | $\Delta E_{ST}$[a] [eV] | $\tau(S_1)$[a] [ns] | $\tau(T_1)$[a] [μs] | $\tau$(TADF)[b] [μs] |
|---|---|---|---|---|
| **1** | 0.18 | 40 | 660 | 134 |
| **2** | 0.13 | 44 | 403 | 23 |

[a] From the fit of Eq. 1. [b] Measured at T = 298 K.

**Table S3.** Crystal data and structure refinement for the cuprous complexes

| Complex | **1**•0.5($C_4H_{10}O$) | **2** |
|---|---|---|
| Empirical formula | $C_{58}H_{49}BCuF_4N_4O_{0.5}P_2$ | $C_{56}H_{42}BCuF_4N_4OP_2$ |
| Formula weight | 1022.30 | 999.23 |
| Crystal system | monoclinic | monoclinic |
| Space group | P2(1)/n | P2(1)/n |
| a (Å) | 26.6146(8) | 13.5909(7) |
| b (Å) | 14.2867(3) | 22.0914(9) |
| c (Å) | 27.5760(7) | 15.8659(7) |
| α (deg) | 90.00 | 90.00 |
| β (deg) | 99.038(3) | 92.711(3) |
| γ (deg) | 90.00 | 90.00 |
| V ($Å^3$) | 10355.2(5) | 4758.3(4) |
| Z | 8 | 4 |
| $\rho_{calc}$ (g $cm^{-3}$) | 1.311 | 1.395 |
| μ ($mm^{-1}$) | 1.650 | 0.588 |
| F(000) | 4232 | 2056 |
| λ (Å) | 1.54178 | 0.71073 |
| Reflections collected/unique | 56480/21484 | 36580/10619 |
| $R_{int}$ | 0.0345 | 0.0353 |
| Θ range (deg) | 2.51-77.23 | 2.14-27.48 |
| GOF on $F^2$ | 1.022 | 1.007 |
| $R_1/wR_2$ [$I \geq 2\sigma(I)$] | 0.0616/0.1779 | 0.0568/0.1709 |
| $R_1/wR_2$ (all data) | 0.0757/0.2007 | 0.0673/0.1827 |

**Table S4.** Selected bond length (Å) and bond angles (deg) for the cuprous complexes

| Complex | **1** | **2** |
|---|---|---|
| Cu-$N_1$ | 2.116(2) | 2.078(2) |
| Cu-$N_3$ | 2.168(2) | 2.138(2) |
| Cu-$P_1$ | 2.2655(8) | 2.2277(7) |
| Cu-$P_2$ | 2.2781(8) | 2.2613(7) |
| $N_1$-Cu-$N_3$ | 77.38(9) | 78.02(9) |
| $P_1$-Cu-$P_2$ | 118.83(3) | 119.94(3) |
| $N_1$-Cu-$P_1$ | 118.17(8) | 106.73(7) |
| $N_1$-Cu-$P_2$ | 99.49(8) | 107.71(7) |
| $N_3$-Cu-$P_1$ | 113.75(6) | 130.75(6) |
| $N_3$-Cu-$P_2$ | 120.68(6) | 103.67(6) |
| ∑metallacycle | 537.29 | 538.58 |

**Table S5.** Orbital transition analyses for lower-lying transitions of **1**.

| States | $\lambda_{cal}$ (nm) | oscillator strength f | Contribution | MLCT (%) |
|---|---|---|---|---|
| $S_1$ | 365.23 | 0.0569 | HOMO→LUMO (68.2%) | 0.00 |
| $S_2$ | 351.27 | 0.0514 | HOMO-1→LUMO (68.1%) | 29.51 |
| $S_3$ | 335.10 | 0.0010 | HOMO-2→LUMO (68.9%) | 0.00 |
| $S_4$ | 330.16 | 0.0914 | HOMO→LUMO+1 (66.2%) | 0.00 |
| $S_5$ | 327.83 | 0.0107 | HOMO-3→LUMO (67.2%) | 35.16 |
| $T_1$ | 393.49 | 0.0000 | HOMO-2→LUMO+2 (42.4%) | 0.00 |
| $T_2$ | 388.76 | 0.0000 | HOMO→LUMO (61.4%) | 2.16 |
| $T_3$ | 382.41 | 0.0000 | HOMO→LUMO+1 (51.4%) | 3.92 |
| $T_4$ | 369.90 | 0.0000 | HOMO-1→LUMO (57.6%) | 21.13 |
| $T_5$ | 352.59 | 0.0000 | HOMO→LUMO+2 (49.4%) | 0.00 |

**Table S6.** Orbital transition analyses for lower-lying transitions of **2**.

| States | λ (nm) | oscillator strength f | Contribution | MLCT (%) |
|---|---|---|---|---|
| $S_1$ | 367.27 | 0.0478 | HOMO→LUMO (65.0%) | 29.28 |
| $S_2$ | 361.90 | 0.0677 | HOMO-1→LUMO (65.1%) | 3.78 |
| $S_3$ | 332.85 | 0.0010 | HOMO-2→LUMO (63.9%) | 4.77 |
| $S_4$ | 330.19 | 0.0082 | HOMO-3→LUMO (57.7%) | 28.58 |
| $S_5$ | 328.05 | 0.0227 | HOMO→LUMO+1 (68.6%) | 32.58 |
| $T_1$ | 395.29 | 0.0000 | HOMO→LUMO (48.5%) | 16.29 |
| $T_2$ | 392.66 | 0.0000 | HOMO-2→LUMO+3 (41.8%) | 0.00 |
| $T_3$ | 386.14 | 0.0000 | HOMO-1→LUMO (51.7%) | 6.88 |
| $T_4$ | 376.86 | 0.0000 | HOMO-1→LUMO+1 (49.8%) | 9.38 |
| $T_5$ | 352.67 | 0.0000 | HOMO -1→LUMO+3 (50.4%) | 0.00 |

## Reference

1 H. Yersin, *Top Curr. Chem.*, 2004**, 241**, 1-26.