Electronic Supplementary Information for

Application of three-coordinate copper(I) complexes with halide ligands in organic light-emitting diodes that exhibit delayed fluorescence

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S1
### Experimental Detail

1. Crystal Structure determination

**Table S1** Crystallographic data for 5

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>formula</td>
<td>C₄₂H₄₈BrCuP₂</td>
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<tr>
<td>formula weight</td>
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<tr>
<td>cryst syst</td>
<td>Orthorhombic</td>
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<td>Pna2₁</td>
</tr>
<tr>
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<td>20.5325(19)</td>
</tr>
<tr>
<td>b / Å</td>
<td>9.3801(9)</td>
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<td>c / Å</td>
<td>19.4895(15)</td>
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<tr>
<td>V / Å³</td>
<td>1679.05 (4)</td>
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<tr>
<td>Z</td>
<td>4</td>
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<tr>
<td>dₐcad / g cm⁻³</td>
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</tr>
<tr>
<td>T / K</td>
<td>90(2)</td>
</tr>
<tr>
<td>radiation</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>(λ = 0.71073 Å)</td>
<td></td>
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<tr>
<td>µ / cm⁻¹</td>
<td>1.763</td>
</tr>
<tr>
<td>diffractometer</td>
<td>Rigaku AFC-8</td>
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</tr>
<tr>
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<td>indep reflns</td>
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<tr>
<td>(Rint = 0.0394)</td>
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<td>no. of param refined</td>
<td>415</td>
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<tr>
<td>R₁, wR² (I &gt; 2σ I)</td>
<td>0.0342, 0.0619</td>
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<tr>
<td>S</td>
<td>0.979</td>
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</table>

[a] R₁ = Σ||F₀| – |F₁||/Σ|F₀|, [b] wR² = [Σw(|F₀| – |F₁|)²/Σw|F₀|²]¹/²
2. NMR Experiments

Figure S1. $^1$H NMR spectrum of 4 in CD$_2$Cl$_2$ at 220 K.

Figure S2. $^{13}$C {$^1$H} NMR spectrum of 4 in CD$_2$Cl$_2$ at 220 K.
Figure S3. $^{31}$P {$^1$H} NMR spectrum of 4 in CD$_2$Cl$_2$ at 220 K.

Figure S4. $^1$H NMR spectrum of 5 in CD$_2$Cl$_2$ at 220 K.
Figure S5. $^{13}$C {${}^1$H} NMR spectrum of 5 in CD$_2$Cl$_2$ at 220 K.

Figure S6. $^{31}$P {${}^1$H} NMR spectrum of 5 in CD$_2$Cl$_2$ at 220 K.
3. Temperature dependence of lifetime

[Fitting procedure A for 1 and 4]

\( \tau_1 \) (decay time from of the T\(_1\) state), \( \tau_5 \) (decay time of the prompt fluorescence), and \( \Delta E(S_1 - T_1) \) (activation energy) were determined from a fit of Eq. 1 to measured \( \tau_{av} \) (25 points) by least-square method.

[Fitting procedure B for 2, 3, and 5]

\( \tau_5 \) (decay time of the prompt fluorescence) and \( \Delta E(S_1 - T_1) \) (activation energy) were determined from a fit of Eq. 1 to measured \( \tau_{av} \) (25 points) by least-square method.

**Fig. S7** Temperature dependence of lifetime for 1.
Fig. S8 Temperature dependence of lifetime for 3. The $\tau_T = 102 \, \mu s$ measured at 77 K was used for the curve fitting by eq. 1.

Fig. S9 Temperature dependence of lifetime for 4.
Fig. S10 Temperature dependence of lifetime for 5. The $t_1 = 909 \mu s$ measured at 77 K was used for the curve fitting by eq. 1.

\[
\tau_{av} = \frac{3 + \exp(-\Delta E(S_1 - T_1)/k_B T)}{3/\tau_1 + 1/\tau_S \exp(-\Delta E(S_1 - T_1)/k_B T)}
\]

$\tau_1 = 909 \mu s$ 

$\Delta E(S_1 - T_1) = 710 \text{ cm}^{-1}$

$\tau_S = 123 \text{ ns}$

Fig. S11 Optimized core structures of 1 in the ground state ($S_0$), the singlet ($S_1$) and the triplet ($T_1$) excited states.
**Fig. S12** Optimized core structures of 2 in $S_0$, $S_1$, and $T_1$.

**Fig. S13** Optimized core structures of 3 in $S_0$, $S_1$, and $T_1$.

**Fig. S14** The sum of the angles around P1 and P2 in each optimized structure of 1.
Fig. S15 The sum of the angles around P1 and P2 in each optimized structure of 3.

Fig. S16 (A) The molecular structure of 3 determined using X-ray structural analysis. (B) The optimized $S_0$ structure of 3.
Table S2 Doping concentration dependence of PLQE for 2 in mCP; \( \lambda_{\text{exc}} = 355 \text{ nm} \).

6. Luminance-Current Efficiency Characteristic

<table>
<thead>
<tr>
<th>Doping concentration (wt%)</th>
<th>5%</th>
<th>10%</th>
<th>20%</th>
<th>100%</th>
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</thead>
<tbody>
<tr>
<td>PLQE / %</td>
<td>65</td>
<td>71</td>
<td>61</td>
<td>38</td>
</tr>
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</table>

Fig. S17 Luminance-Current Efficiency Characteristic