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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Contents

Experimental Detail

1. Crystal Structure determination

Table S1 Crystallographic data for **5**

	5
formula	$C_{42}H_{48}BrCuP_2$
formula weight	758.24
cryst syst	Orthorhombic
space group	$Pna2_1$
a / Å	20.5325(19)
b / Å	9.3801(9)
c / Å	19.4895(15)
V / Å^3	1679.05 (4)
Z	4
d_{calcd} / g cm^{-3}	1.342
T / K	90(2)
radiation	Mo Kα
	(λ = 0.71073 Å)
μ / cm^{-1}	1.763
diffractometer	Rigaku AFC-8
max 2θ / deg	60
reflns collcd	24700
indep reflns	9995
	(Rint = 0.0394)
no. of param refined	415
R1,[a] *wR2* ($I > 2\sigma I$)[b]	0.0342, 0.0619
S	0.979

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR2 = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2}$

2. NMR Experiments

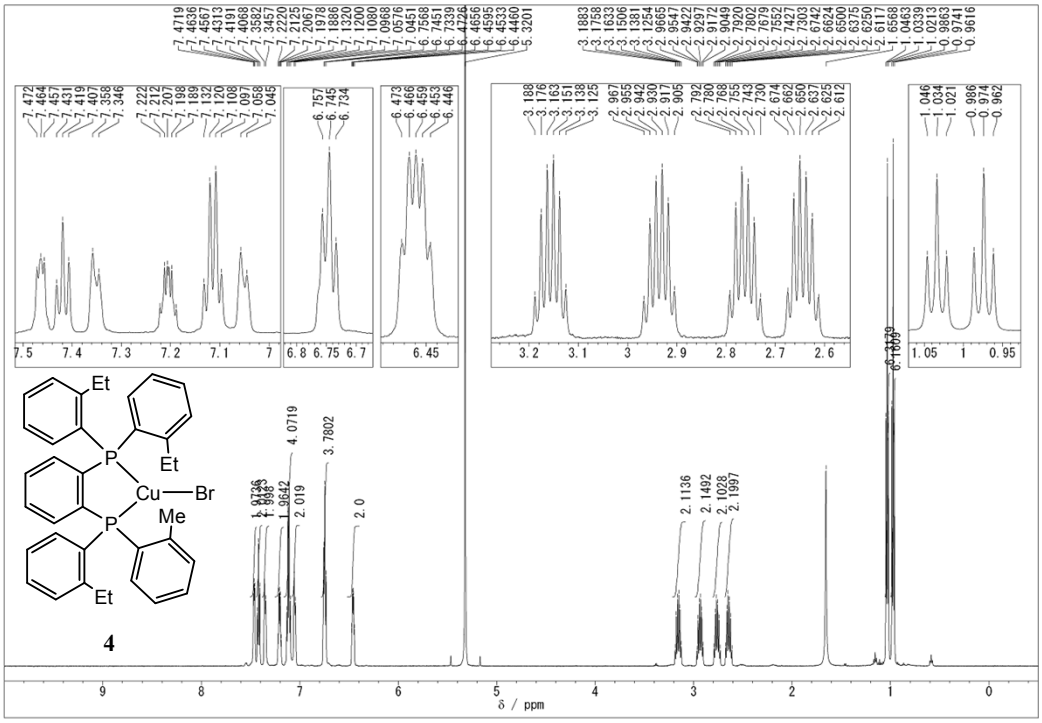


Figure S1. ^{1}H NMR spectrum of **4** in CD_2Cl_2 at 220 K.

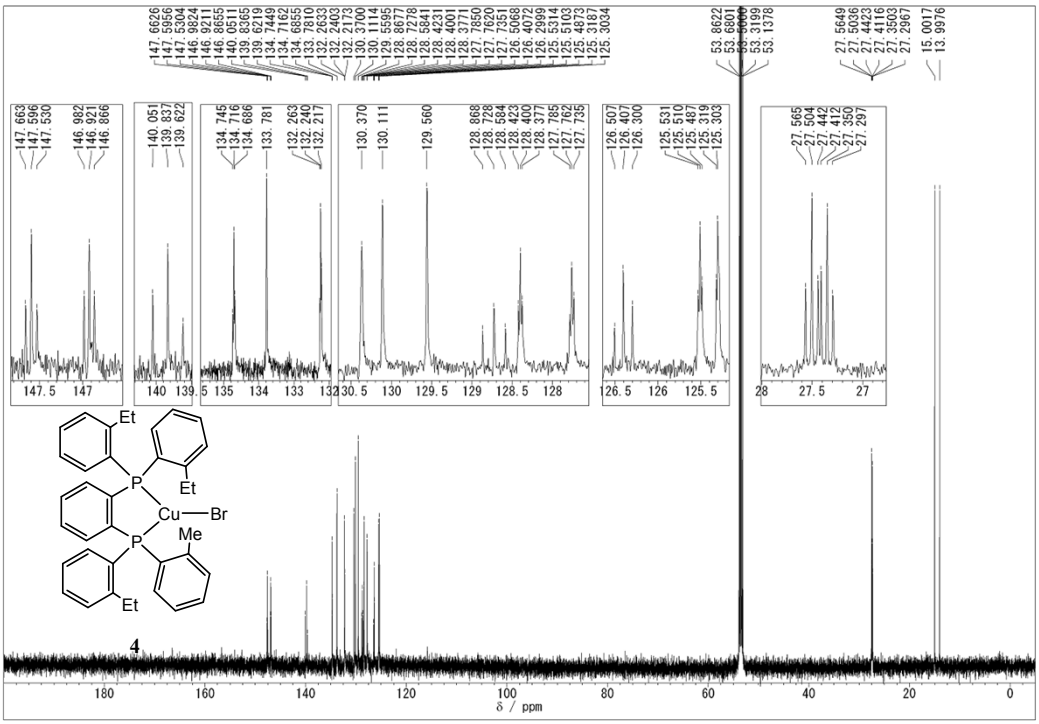


Figure S2. ^{13}C {^{1}H} NMR spectrum of **4** in CD_2Cl_2 at 220 K.

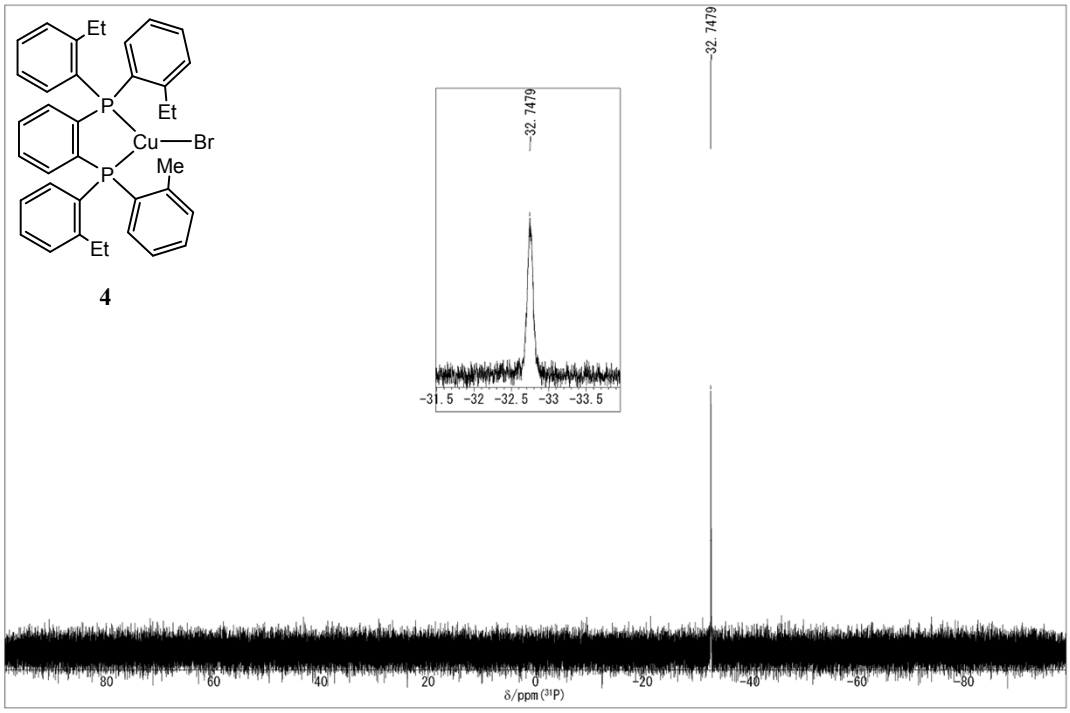


Figure S3. ^{31}P $\{^{1}H\}$ NMR spectrum of **4** in CD_2Cl_2 at 220 K.

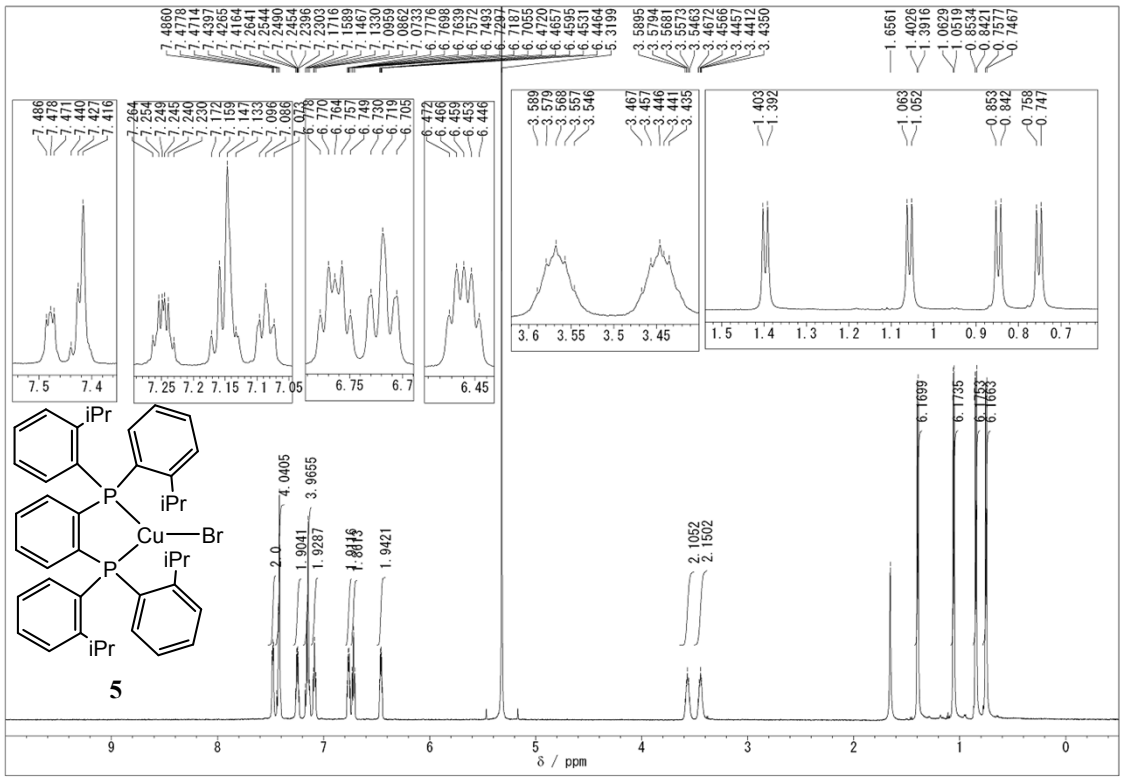


Figure S4. ^{1}H NMR spectrum of **5** in CD_2Cl_2 at 220 K.

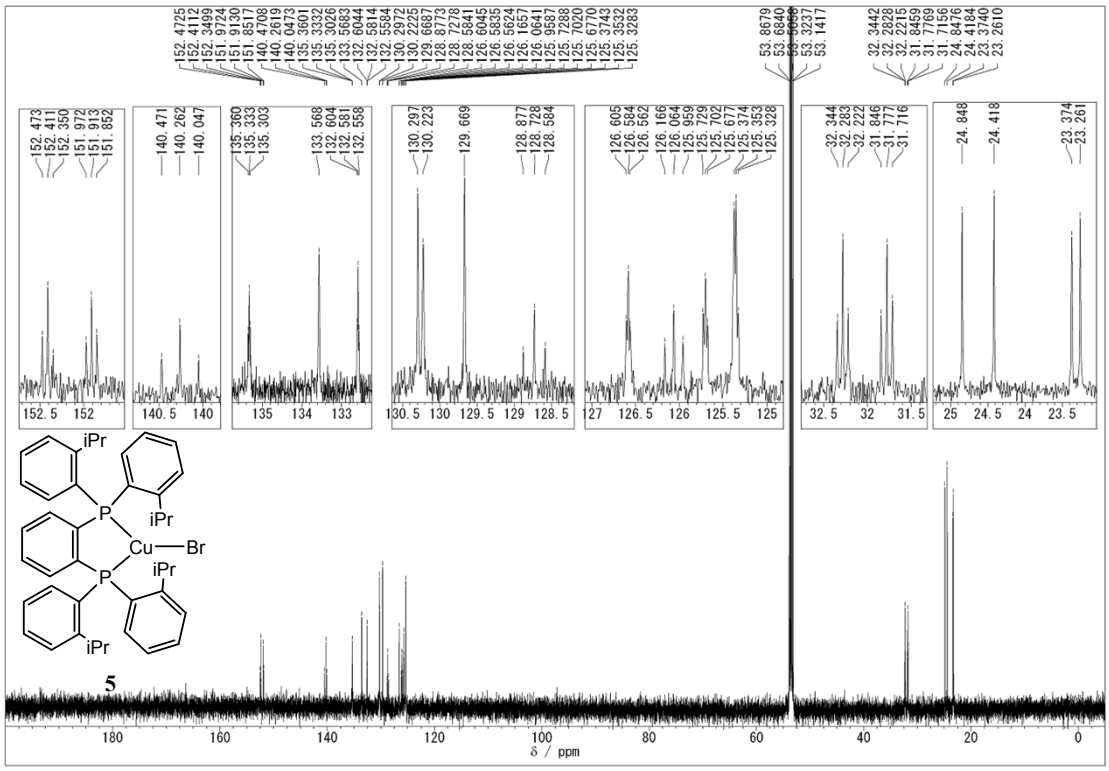


Figure S5. ^{13}C $\{^{1}H\}$ NMR spectrum of **5** in CD_2Cl_2 at 220 K.

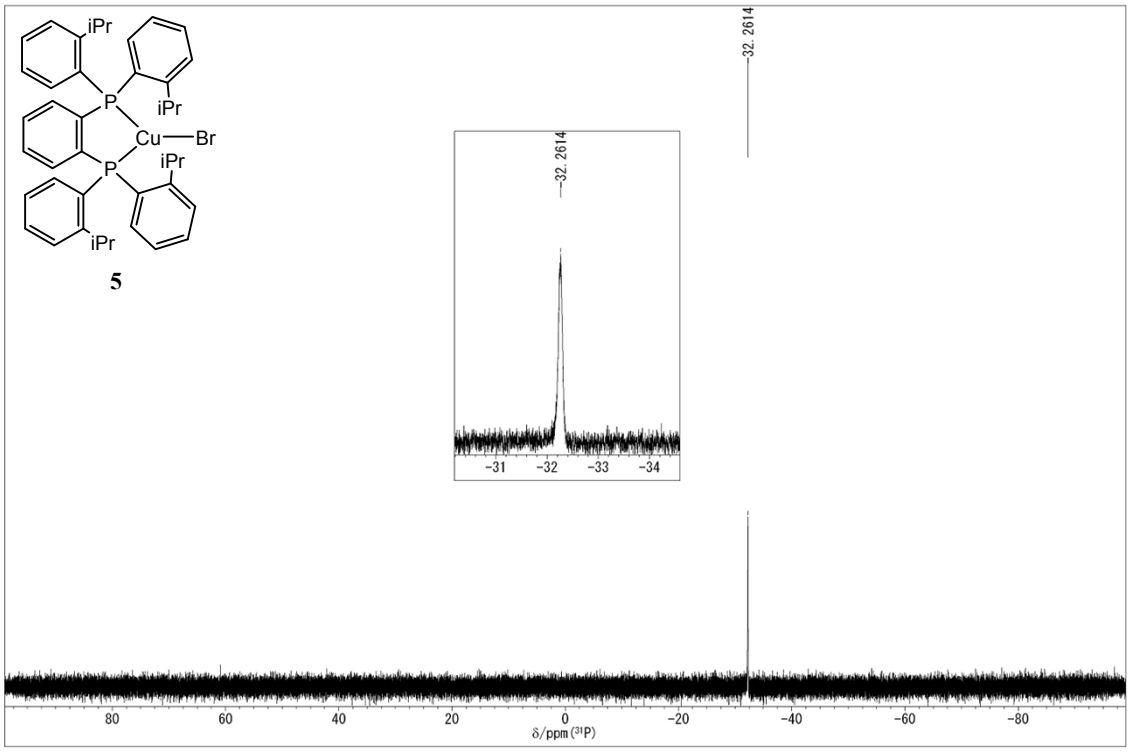


Figure S6. ^{31}P $\{^{1}H\}$ NMR spectrum of **5** in CD_2Cl_2 at 220 K.

3. Temperature dependence of lifetime

[Fitting procedure A for **1** and **4**]

τ_T (decay time from of the T_1 state), τ_S (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 τ_{av} (25 points) by least-square method.

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

τ_S (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 τ_{av} (25 points) by least-square method.

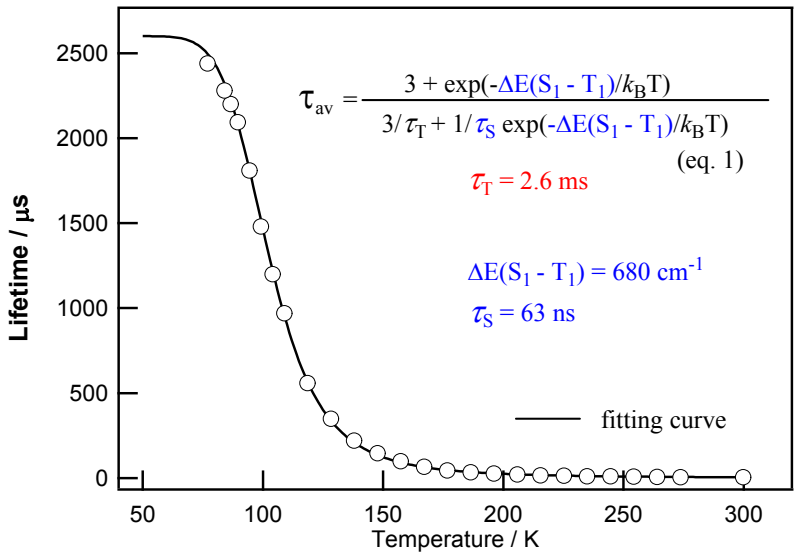


Fig. S7 Temperature dependence of lifetime for **1**.

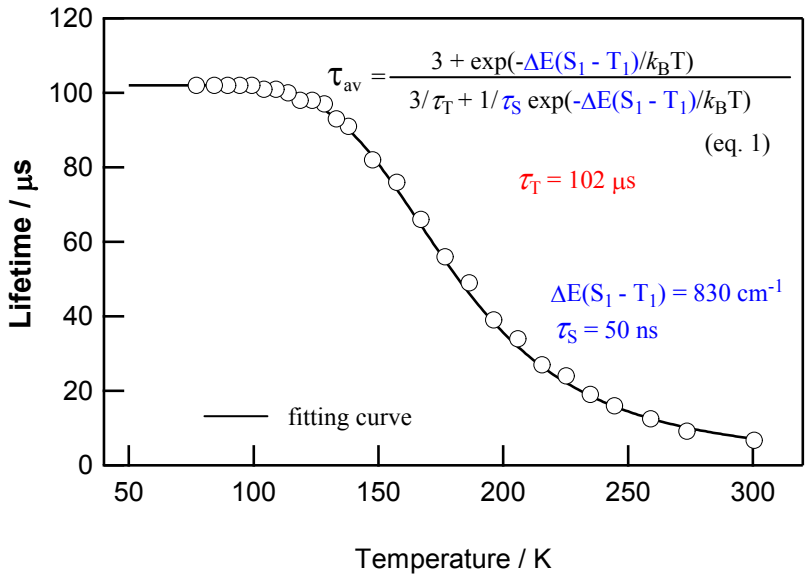


Fig. S8 Temperature dependence of lifetime for **3**. The t_T = 102 μs measured at 77 K was used for the curve fitting by eq. 1.

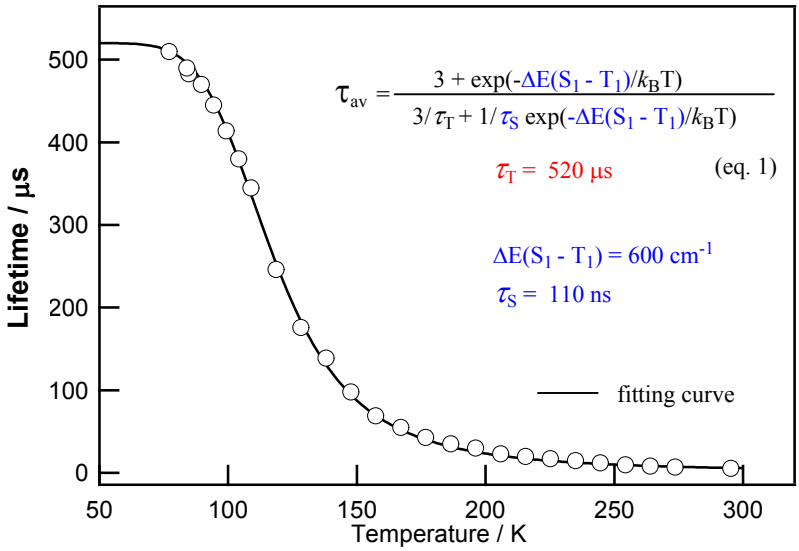


Fig. S9 Temperature dependence of lifetime for **4**.

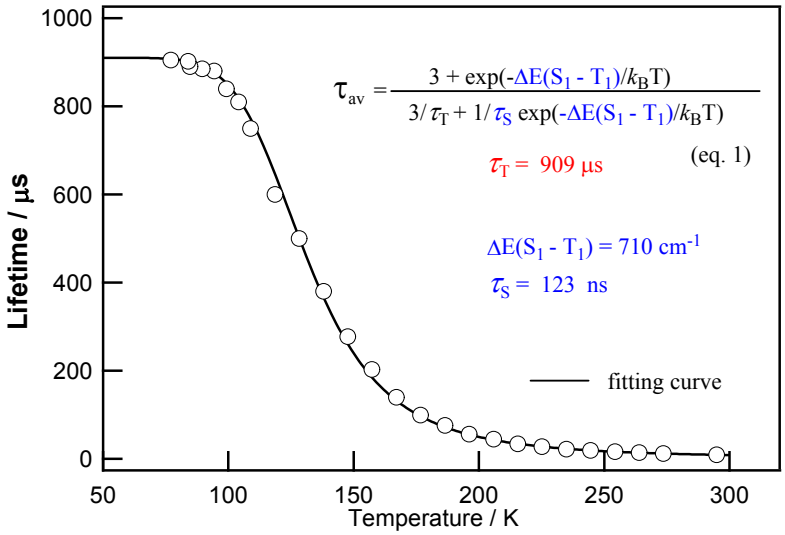
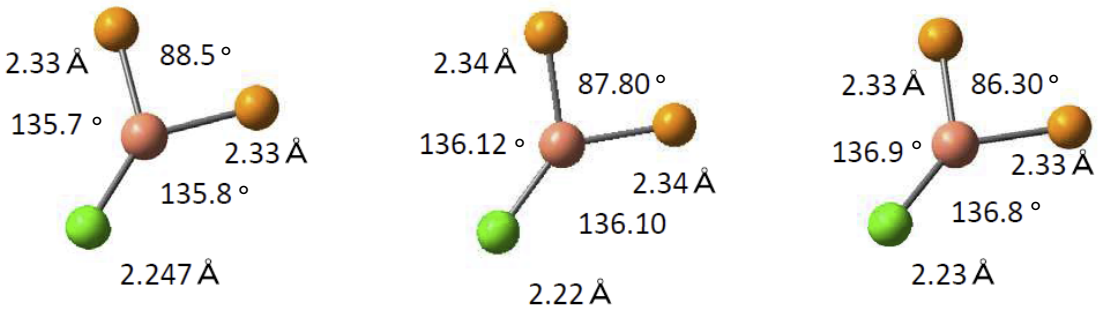
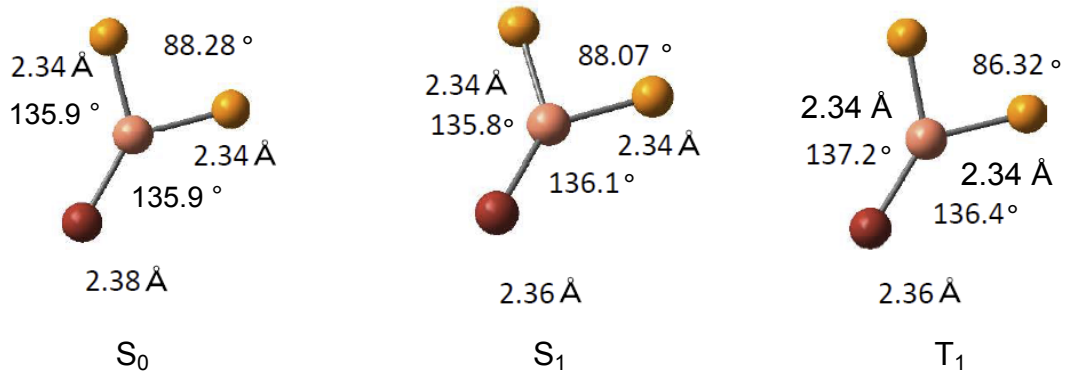


Fig. S10 Temperature dependence of lifetime for **5**. The t_T = 909 μs measured at 77 K was used for the curve fitting by eq. 1.



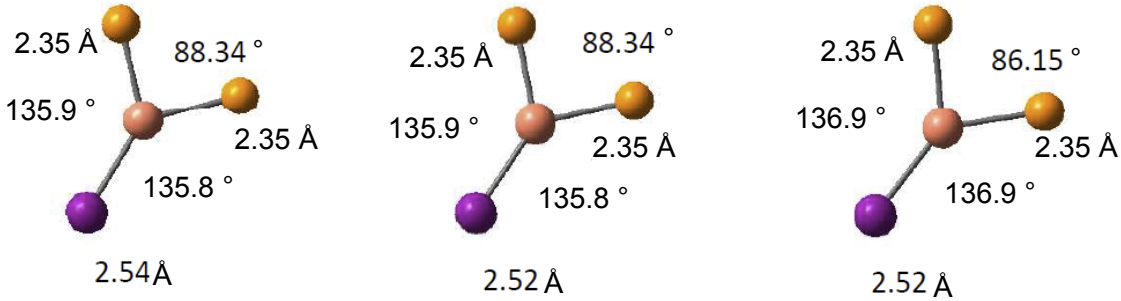
□□□□□ S_0 S_1 T_1

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



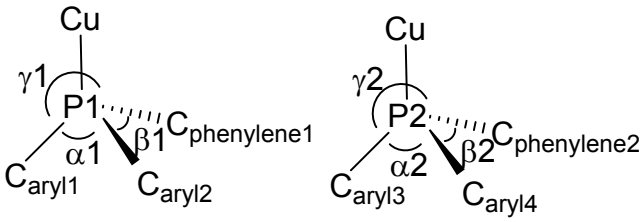
S_0 S_1 T_1

Fig. S12 Optimized core structures of **2** in S_0, S_1, and T_1.



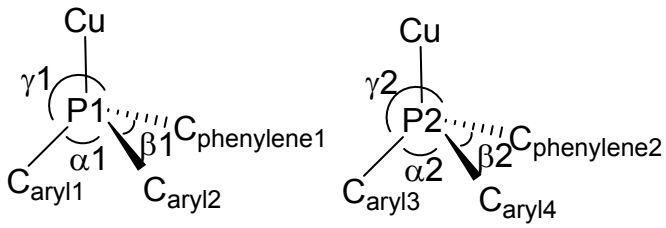
S_0 S_1 T_1

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



	α1 + β1 + γ1	α2 + β2 + γ2
S_0	314.6°	314.6°
S_1	326.0°	326.0°
T_1	328.3°	328.2°

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



	α1 + β1 + γ1	α2 + β2 + γ2
S_0	313.9°	313.9°
S_1	324.4°	324.3°
T_1	327.2°	327.2°

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

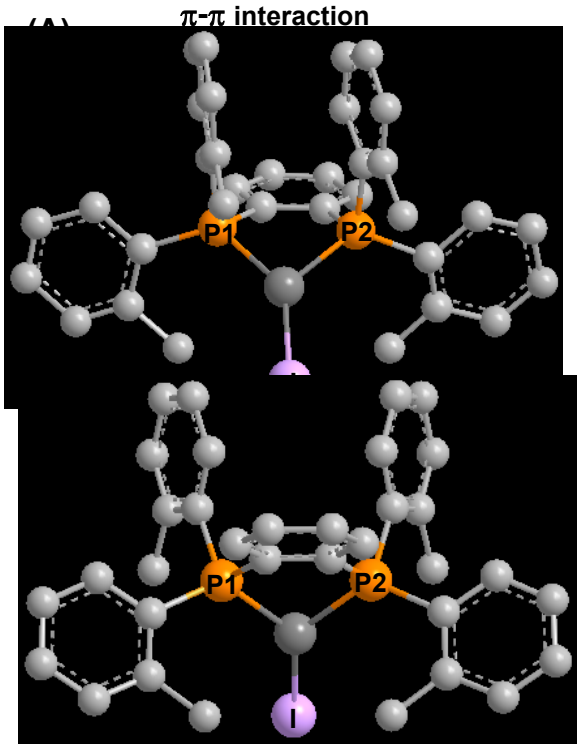


Fig. S16 (A) The molecular structure of **3** determined using X-ray structural analysis. (B) The optimized S_0 structure of **3**.

Doping concentration (wt%)	5%	10%	20%	100%
PLQE / %	65	71	61	38

Table S2 Doping concentration dependence of PLQE for **2** in mCP; λ_{exc} = 355 nm.

6. Luminance-Current Efficiency Characteristic

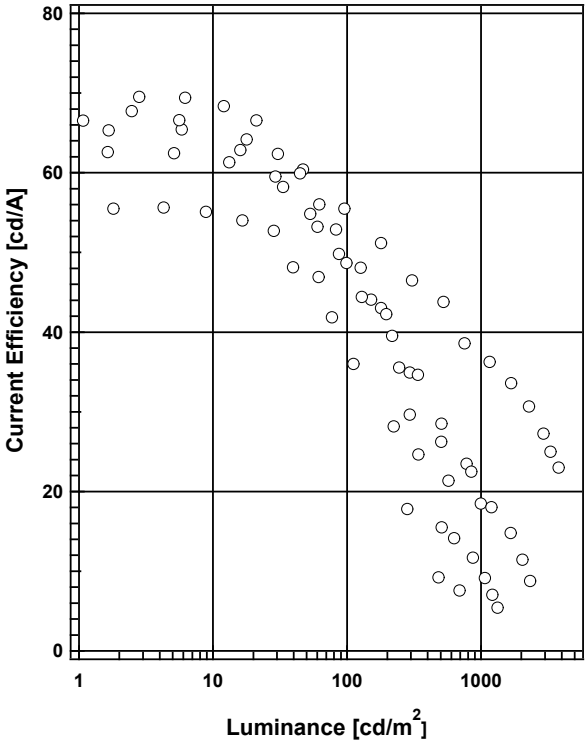


Fig. S17 Luminance-Current Efficiency Characteristic