Supporting Information for

Bright bluish-green emitting Cu(I) complexes exhibiting efficient Thermally Activated Delayed Fluorescence

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S1. General Procedures

All commercially available starting materials were used without any purification. All reactions were performed under a nitrogen atmosphere. The crystal diffraction data were collected by single-crystal X-ray diffraction analysis with graphite monochromatized Mo K_α radiation (λ=0.71073 Å). The structures were obtained by direct methods and refined by full-matrix least squares methods using the SHELXL-97 program package.[1] The crystallographic data of three Cu(I) complexes have been deposited at the Cambridge Crystallographic Data Center. CCDC 2052750 (**1**), 2052752 (**2**) and 2052751 (**3**). Elemental analyses of C, H, and N were carried out with a Elementar Vario El Cube elemental analyzer. UV-Vis absorption spectra were obtained on a Perkin-Elmer lambda 900 UV-Vis spectrometer. Luminescence spectra were carried out on an Edinburgh Instrument F980 fluorescent spectrometer. The luminescence quantum yields were recorded on a Hamamatsu Photonics C11347-11 absolute photoluminescence quantum yield spectrometer.

S2. Synthesis of Materials

The three diimine ligands were synthesized referring to the literature.[2, 3] The Cu(I) complexes were synthesized by mixing $Cu(CH_3CN)_4BF_4$(0.1mmol), POP ligand(0.1mmol) and diimine ligands(0.1mmol) in CH_2Cl_2 at room temperature. After slow diffusion of diethyl ether vapor to the reaction mixture, granular crystals suitable for X-ray single-crystal diffraction measurement were obtained. The pure products of these Cu(I) complexes were obtained by recrystallizing from ether. All the diamine ligands and Cu(I) complexes were characterized by ^{1}H NMR spectra on a Bruker Avance III 500MHz NMR spectrometer.

tBupzmpy: ^{1}H NMR (500 MHz, Chloroform-d) δ 7.61 (t, J = 7.7 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.65 (s, 1H), 2.59 (s, 3H), 1.37 (s, 9H).

Phpzmpy: ^{1}H NMR (500 MHz, Chloroform-d) δ 7.86 (d, J = 7.2 Hz, 2H), 7.65 (t, J = 7.7 Hz, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 7.03 (s, 1H), 2.61 (s, 3H).

Adpzmpy: ^{1}H NMR (500 MHz, Chloroform-d) δ 7.59 (t, J = 7.7 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 6.62 (s, 1H), 2.58 (s, 3H), 2.09 (s, 3H), 2.00 (s, 6H), 1.79 (s, 6H).

Complex [Cu(tBupzmpy)(POP)]BF₄: (colorless crystal, yield: 58mg, 65%). ^{1}H NMR (500 MHz, Methylene Chloride-d2) δ 10.06 (s, 1H), 7.84 (s, 1H), 7.65 (s, 1H), 7.16 (dd, J = 138.6, 38.1 Hz, 27H), 6.75 (s, 2H), 6.52 (s, 1H), 2.29 (s, 3H), 1.84 (s, 9H). ^{31}P NMR (202 MHz, Methylene Chloride-d2) δ -12.54. Elemental analysis: calc for $C_{49}H_{45}BCuF_4N_3OP_2$: C, 65.08; H, 5.01; N, 4.69. Found: C, 67.3; H, 4.58; N, 4.63.

Complex [Cu(Phpzmpy)(POP)]BF₄: (colorless crystal, yield: 72mg, 78%). ^{1}H NMR (500 MHz, Methylene Chloride-d2) δ 10.91 (s, 1H), 7.87 (s, 1H), 7.74 (s, 1H), 7.46 (td, J = 16.4, 15.7, 7.4 Hz, 6H), 7.40 – 7.12 (m, 19H), 7.01 (dd, J = 17.9, 10.4 Hz, 8H), 6.76 (dtd, J = 7.9, 4.0, 1.6 Hz, 2H), 2.19 (s, 3H). ^{31}P NMR (202 MHz, Methylene Chloride-d2) δ -13.27. Elemental analysis: calc for $C_{51}H_{41}BCuF_4N_3OP_2$: C, 66.28; H, 4.47; N, 4.80. Found: C, 67.29; H, 5.06; N, 4.80.

Complex [Cu(Adpzmpy)(POP)]BF₄: (colorless crystal, yield: 83mg, 85%). ^{1}H NMR (500 MHz, Methylene Chloride-d2). δ 9.96 (s, 1H), 7.83 (t, J = 7.8 Hz, 1H), 7.66 (d, J = 7.7 Hz, 1H), 7.40–7.29 (m, 8H), 7.23 (d, J = 9.3 Hz, 9H), 7.14 (d, J = 7.7 Hz, 1H), 7.12–6.98 (m, 12H), 6.75 (s, 2H), 6.51 (s, 1H), 2.29 (s, 3H), 2.06–2.01 (m, 3H), 1.83–1.70 (m, 12H). ^{31}P NMR (202 MHz, Methylene Chloride-d2). δ -13.08. Elemental analysis: calc for $C_{55}H_{51}BCuF_4N_3OP_2$: C, 67.24; H, 5.23; N, 4.48. Found: C, 67.29; H, 5.22; N, 4.48.

S3. Crystal parameters and refinement data

Table S1 Crystal parameters and refinement data of complexes **1-3**

Complex	1	2	3
Empirical formula	$C_{49}H_{45}BCuF_4N_3OP_2$	$C_{51}H_{41}BCuF_4N_3OP_2$	$C_{55}H_{51}BCuF_4N_3OP_2$
Formula weight	904.18	924.17	982.29
Crystal system	triclinic	monoclinic	triclinic
Space group	P-1	P21	P-1
a/ Å	9.824(4)	9.673(4)	10.105(4)

b/ Å	13.161(5)	16.603(5)	13.447(5)
c/ Å	18.423(6)	14.007(6)	20.983(8)
α/°	96.354(2)	90	89.808(1)
β/°	97.197(2)	97.6950(1)	77.186(1)
γ/°	103.994(1)	90	69.217(1)
Volume/?3	2268.37(2)	2229.21(2)	2590.33(2)
Z	2	2	2
ρcalcg/cm3	1.324	1.377	1.259
F(000)	936	952	1020
Crystal size/mm^3	0.32 × 0.21 × 0.19	0.15 × 0.15 × 0.08	0.17 × 0.15 × 0.15
2Θ/°	5.1 to 55.08	4.91 to 55.01	3.67 to 55.09
h	-12 ≤ h ≤ 12	-12 ≤ h ≤ 12	-13 ≤ h ≤ 13
k	-17 ≤ k ≤ 17	-21 ≤ k ≤ 21	-17 ≤ k ≤ 17
l	-23 ≤ l ≤ 23	-18 ≤ l ≤ 17	-27 ≤ l ≤ 27
Reflections collected	70868	65560	116767
Independent reflections	10382	10115	11899
Data/restraints/paramete	10382/0/554	10115/1/569	11899/0/605
G.O.F	1.053	1.047	1.086
R_1,wR_2 [I>=2σ (I)]	0.0410, 0.1117	0.0393, 0.0876	0.0515, 0.1529
R_1,wR_2 [all data]	0.0452, 0.1151	0.0466, 0.0936	0.0560, 0.1569
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e·Å$^-$	0.55/-0.51	0.52/-0.41	1.69/-0.73

[a]$R_1=\sum||Fo| - |Fc||/\sum|Fo|$. [b]$wR_2=[\sum w(Fo^2 \_ Fc^2)^2/\sum w(Fo^2)]^{1/2}$

S4. Selected bond distances and angles

Table S2 Selected bond distances [Å] and angles [°] for complexes **1–3**

	1	2	3
bond distances [Å]			
Cu1-P1	2.280(5)	2.256(1)	2.274(6)
Cu1-P2	2.269(5)	2.284(1)	2.271(7)
Cu1-N1	2.127(2)	2.154(3)	2.101(2)
Cu1-N2	2.078(1)	2.081(3)	2.084(2)
angles [°]			
P1-Cu1-P2	115.07(2)	112.39(4)	114.52(2)
N1-Cu1-P1	109.14(4)	120.65(9)	112.04(6)
N1-Cu1-P2	116.52(4)	108.60(9)	114.93(6)
N2-Cu1-P1	114.71(4)	117.14(1)	117.89(6)
N2-Cu1-P2	116.90(4)	114.81(1)	113.09(6)
N2-Cu1-N1	79.44(6)	79.42(1)	79.88(8)

S5. Cyclic voltammetry measurement

Cyclic voltammetry was performed on a BAS Epsilon Electrochemical Analyzer with a gastight single-compartment three-electrode cell. A glassy carbon disk and a platinum wire were used as working and auxiliary electrodes, respectively and the reference electrode was Ag/Ag+ (0.1 M of AgNO$_3$ in CH$_2$Cl$_2$). The CV measurements were performed in anhydrous and nitrogen-saturated dichloromethane solutions with 0.05 M n-tetrabutylammonium perchlorate (TBAP) and 0.05 mM cuprous complexes. The ferrocenium/ferrocene couple was used as an internal standard.
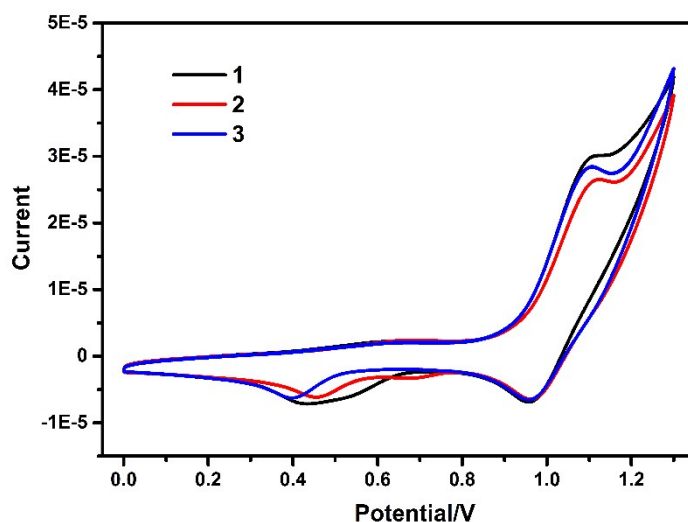

Figure S1 Cyclic voltammograms for the oxidation of complex **1**, **2** and **3**.

S6. Computational Methodology and Results

All the calculations were carried out using the Gaussian 09 program package.[4] The density functional theory (DFT) calculations were used to optimize the ground state geometries of the investigated compounds.[5] A "double-ζ" quality basis set consisting of Hay and Wadt's effffective core potentials (LANL2DZ) was employed for the C, N and H atoms, and a LANL08 basis set was employed for the Cu and P atoms. Time-dependent density functional theory (TD-DFT) calculations were performed at the PBE0 level using the optimized ground state geometries.[6, 7] The electron density diagrams of molecular orbitals were generated using Gauss View program. The partition orbital composition was analyzed by using the Multiwfn 2.4 program.[8]
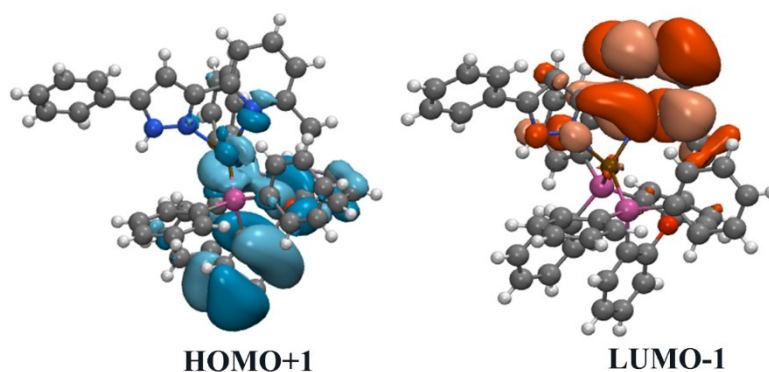

HOMO+1   LUMO-1

Figure S2 The HOMO+1(blue) and LUMO-1(orange) orbital distribution of complex **2**.

Table S3 The orbital composition of HOMO and LUMO orbits for complexes **1–3**

Complex	Orbit	Cu	POP	NN
1	HOMO	30.51%	63.36%	6.13%
	LUMO	3.92%	5.71%	90.37%
2	HOMO	32.60%	59.86%	7.54%
	LUMO	3.67%	5.52%	90.80%
3	HOMO	30.67%	62.36%	6.97%
	LUMO	4.26%	5.94%	89.80%

S7. TGA curves

The TGA test were performed on a Mettler Telodo synchronous thermal analyser with a 10 ℃/min heating rate at the flowing N_2 atmosphere. All of these samples prepared for experiment have been dried for 2 hours at 90℃.
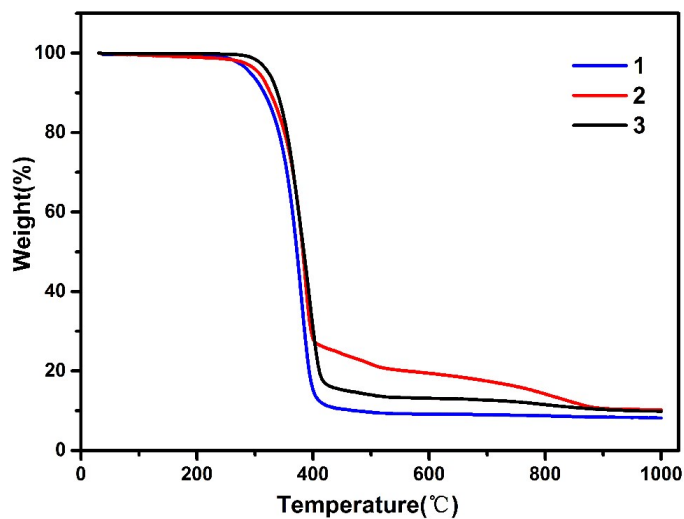

Figure S3 TGA curves of complex **1**-**3**.

S8. The dihedral angles θ between plane N1–Cu(1)–N2 and P1–Cu(1)–P2 of complexes 1 and 2 in different viewing directions
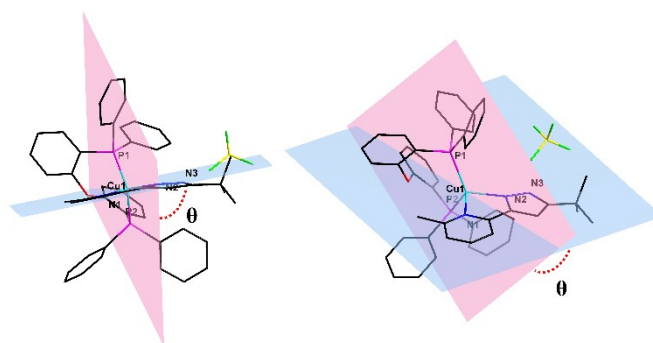

Figure S4 The dihedral angles θ between plane N1–Cu(1)–N2 and P1–Cu(1)–P2 of complexes **1** in different viewing directions.
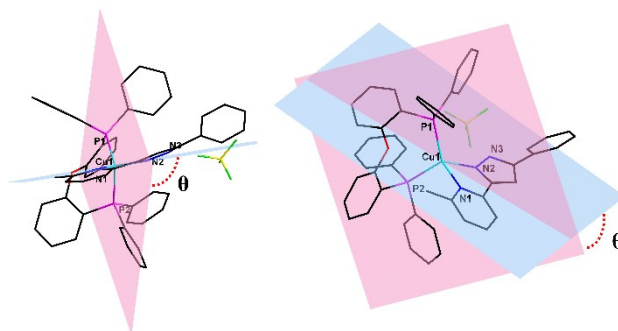

Figure S5 The dihedral angles θ between plane N1–Cu(1)–N2 and P1–Cu(1)–P2 of complexes **2** in different viewing directions.

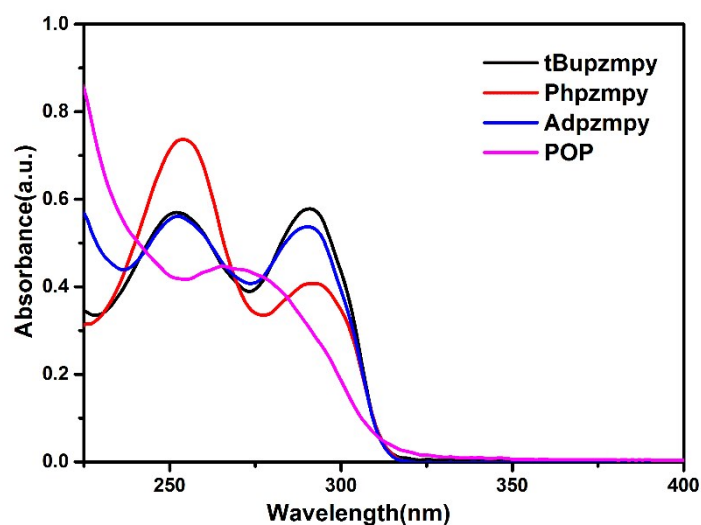## S9. UV-vis spectra of ligands in degassed CH_2Cl_2

Figure S6 UV-vis spectra of ligands in degassed CH_2Cl_2.

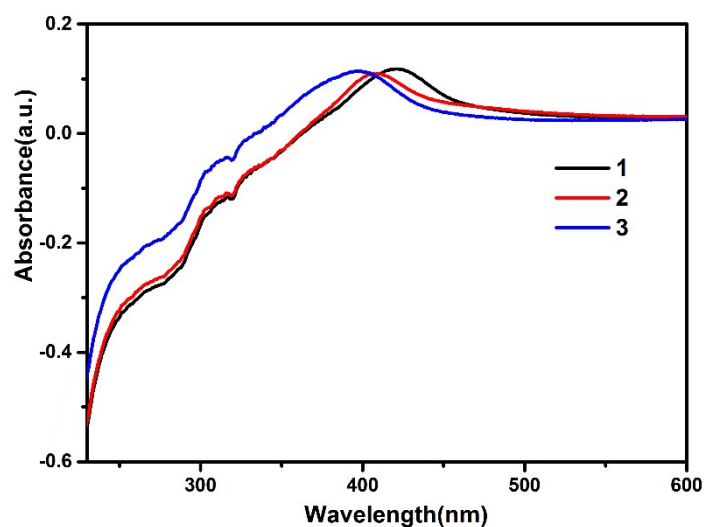## S10. Solid state UV-Vis absorption spectra of complexes 1-3

Figure S7 Solid state UV-Vis absorption spectra of complexes **1-3**.

Notes and references

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