Supplementary Information for

Experimental and theoretical studies of highly emissive dinuclear Cu(I) halide complexes with delayed fluorescence

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1. Crystal Structure Determination

Table S1 Selected crystallographic data of copper complexes **1-3.**

Compound reference	**1**	**2**	**3**
Chemical formula	$C_{64}H_{56}Cu_2I_2P_4$	$C_{64}H_{56}Br_2Cu_2P_4$	$C_{64}H_{56}Cl_2Cu_2P_4$
Formula Mass	1329.85	1235.87	1146.95
Crystal system	monoclinic	monoclinic	monoclinic
a/Å	21.9969(4)	19.6495(8)	19.3870(5)
b/Å	10.4072(2)	10.3582(3)	10.4225(2)
c/Å	24.4603(4)	28.0465(1)	27.8742(9)
α/°	90.00	90.00	90.00
β/°	104.156(2)	110.437(4)	109.480(3)
γ/°	90.00	90.00	90.00
Unit cell volume/Å^3	5429.56(17)	5352.5(3)	5309.9(2)
Temperature/K	100(2)	100(2)	100(2)
Space group	*P2/n*	*C2/c*	*C2/c*
No. of formula units per unit cell, *Z*	4	4	4
No. of reflections measured	21433	17959	18564
No. of independent reflections	11095	5428	5383
R_{int}	0.0267	0.0315	0.0319
Final R_1 values ($I > 2\sigma(I)$)	0.0388	0.0365	0.0355
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1037	0.0936	0.0965
Final R_1 values (all data)	0.0441	0.0424	0.0434
Final $wR(F^2)$ values (all data)	0.0991	0.0901	0.0910
Goodness of fit on F^2	1.031	1.060	1.038
CCDC reference numbers	1057114	1057120	1057182

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

2. Theoretical Studies

Table S2 Composition of HOMO, HOMO-1, LUMO, and LUMO+1 of complex **1**-**3** in the structure determined by X-ray analysis.

		Cu	X	P	C
Compound **1**	HOMO-1	38.915396%	20.883548%	20.617488%	19.583569%
	HOMO	28.720633%	26.644146%	26.798742%	17.836479%
	LUMO	2.145174%	0.244652%	9.239101%	88.371072%
	LUMO+1	4.214277%	0.284196%	9.069996%	86.431532%
Compound **2**	HOMO-1	42.531232%	8.711976%	26.384973%	22.371819%
	HOMO	31.494948%	18.665268%	30.900684%	18.939099%
	LUMO	3.457672%	0.113562%	9.509203%	86.919563%
	LUMO+1	3.555854%	0.214046%	8.443582%	87.786519%
Compound **3**	HOMO-1	43.756072%	6.129325%	27.956252%	22.158350%
	HOMO	32.665819%	17.214855%	31.232005%	18.887320%
	LUMO	3.656629%	0.070245%	11.297727%	84.975399%
	LUMO+1	3.495814%	0.204651%	8.262753%	88.036782%

Table S3 Calculated energy levels, oscillator strengths (f), and orbital transition analyses for selected lower-lying transitions for complexes **1–3**

	states	λ_{cal}(nm)	f	assignments	MLCT	XLCT(P→π*)
1	S1	370.63	0.0204	HOMO→LUMO (82%)	27.0%	23.5% (17.2%)
				HOMO-1→LUMO+1 (13%)		
	S2	370.19	0.0085	HOMO→LUMO +1(82%)	24.6%	23.6%(17.5%)
				HOMO-1→LUMO (12%)		
	S3	361.28	0.0417	HOMO→LUMO +2(88%)	24.6%	23.5%(17.5%)
	S4	358.03	0.0085	HOMO→LUMO+3 (76%)	23.0%	23.4%(11.8%)
				HOMO-1→LUMO+2 (13%)		
	S5	349.88	0.0004	HOMO-1→LUMO+1 (82%)	36.2%	23.1%(-5.7%)
				HOMO→LUMO (12%)		
	T1	384.40	0	HOMO-1→LUMO+1 (18%)	26.3%	20.1%(19.3%)
			0	HOMO→LUMO (62%)		
	T2	383.75	0	HOMO-1→LUMO (21%)	25.3%	20.2%(19.4%)
			0	HOMO→LUMO+1 (65%)		
2	S1	370.38	0.0395	HOMO-1→LUMO+1 (25%)	28.6%	16.5%(22.0%)
				HOMO→LUMO (68%)		
	S2	370.06	0.0052	HOMO-1→LUMO (22%)	27.5%	16.5%(22.2%)
				HOMO→LUMO+1 (70%)		
	S3	365.00	0.0292	HOMO-1→LUMO+3 (13%)	28.2%	17.3%(11.3%)
				HOMO→LUMO+2 (76%)		
	S4	360.60	0.0144	HOMO-1→LUMO+2 (21%),	25.7%	16.3%(15.6%)
				HOMO→LUMO+3 (63%)		
	S5	349.91	0.0054	HOMO-1→LUMO+1 (34%)		
				HOMO→LUMO+4 (34%)		
				HOMO-1→LUMO+3 (16%)		
	T1	388.33	0	HOMO-1→LUMO+1 (20%)	26.6%	14.5%(21.1%)
			0	HOMO→LUMO (57%)		
	T2	386.87	0	HOMO-1->LUMO (33%)	27.4%	14.1%(22.9%)
			0	HOMO->LUMO+1 (53%)		
3	S1	368.97	0.0325	HOMO-1→LUMO+1 (39%)	29.7%	14.9%(22.1%)
				HOMO→LUMO (37%)		
				HOMO→LUMO+2 (22%)		
	S2	368.89	0.0067	HOMO-1→LUMO (20%)	28.8%	14.8%(22.5%)
				HOMO→LUMO+1 (59%)		
				HOMO-1→LUMO+2 (18%)		
	S3	365.80	0.036	HOMO-1→LUMO+3 (22%)	29.7%	15.8%(12.0%)
				HOMO→LUMO+2 (44%)		

				HOMO-1→LUMO (31%)		
	S4	362.83	0.0164	HOMO→LUMO+3 (48%)	40.2%	3.6%(11.9%)
				HOMO-1→LUMO (24%)		
				HOMO-1→LUMO+2 (20%)		
	S5	350.26	0.0084	HOMO→LUMO+4 (39%)	14.2%	16.7%(19.1%)
				HOMO-1→LUMO+3 (22%)		
				HOMO→LUMO (19%)		
				HOMO-1→LUMO+1 (15%)		
	T1	388.43	0	HOMO→LUMO (50%)	21.5%	13.2%(15.9%)
			0	HOMO-1→LUMO+3 (19%)		
				HOMO-1→LUMO+1 (14%)		
	T2	387.02	0	HOMO-1→LUMO (41%)	35.8%	4.5%(16.8%)
			0	HOMO→LUMO+1(26%)		
				HOMO→LUMO+3 (19%)		

Table S4 Compositions of hole and electron in the S1 state of **1**–**3**. (X-ray crystal structure)

		Cu	X	P	C
Compound **1**	electron	29.663528%	23.936657%	28.246666%	18.153149%
	hole	2.693347%	0.385942%	11.045402%	85.875309%
	difference	27.0%	23.5%	17.2%	-69.7%
Compound **2**	electron	32.054545%	16.782287%	32.102274%	19.060894%
	hole	3.532379%	0.240678%	10.133328%	86.093615%
	difference	28.5%	16.5%	22.0%	-69.0%
Compound **3**	electron	33.363023%	15.076964%	32.493719%	19.066295%
	hole	3.639579%	0.241130%	10.367895%	85.751396%
	difference	29.7%	14.8%	22.1%	-69.8%

Table S5 Compositions of hole and electron in the T1 state of **1**–**3**. (X-ray crystal structure)

		Cu	X	P	C
Compound **1**	electron	28.052301%	20.339825%	30.636054%	20.971820%
	hole	1.747455%	0.185693%	11.385343%	86.681509%
	difference	26.3%	19.2%	19.3%	-65.7%
Compound **2**	electron	29.696043%	14.576849%	33.827229%	21.899879%
	hole	3.098879%	0.051751%	14.680360%	82.169011%
	difference	26.6%	14.5%	19.1%	-60.3%
Compound **3**	electron	30.546170%	13.540376%	33.873636%	22.039818%
	hole	3.051156%	0.193658%	18.005569%	78.749616%
	difference	27.5%	13.3%	15.8%	-56.7%

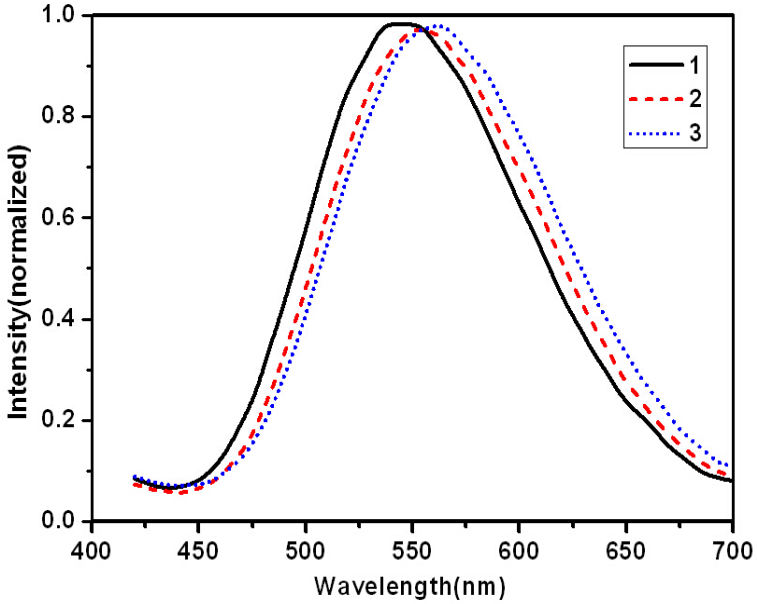

Fig. S1 Emission spectra of cuprous complexes and free ligand in degassed CH_2Cl_2 ($c = 1\times10^{-5}$) at room temperature.

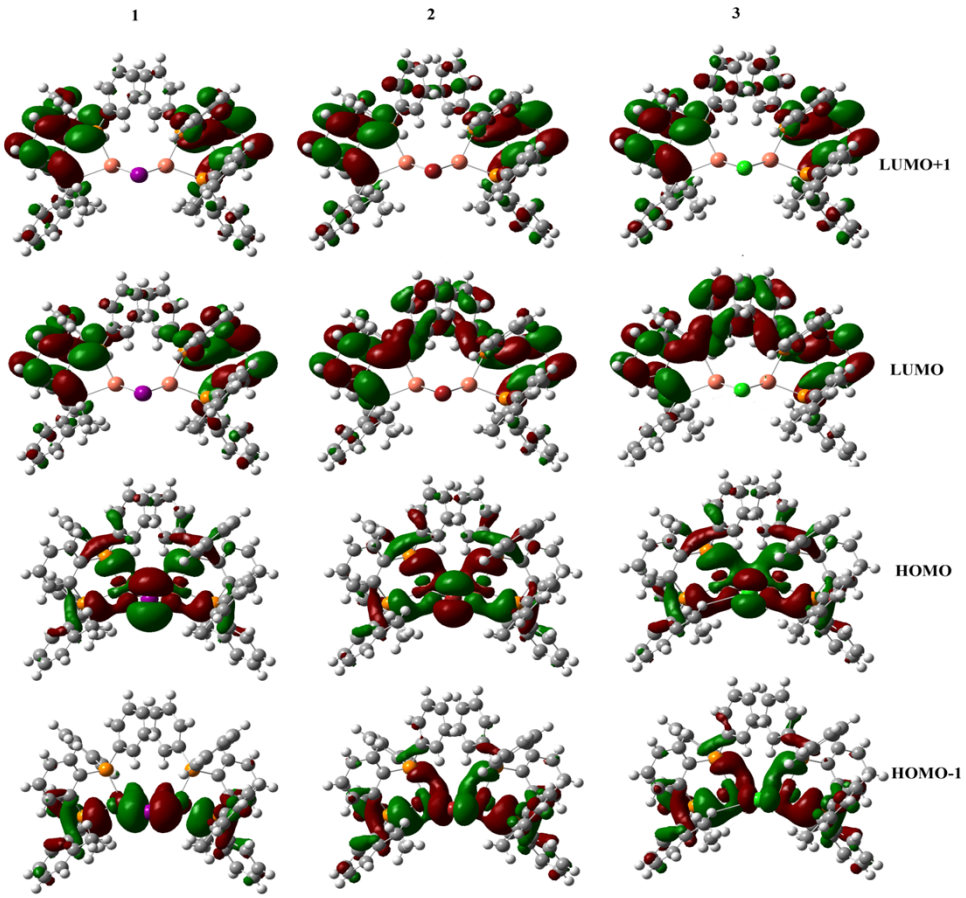

Fig. S2 HOMO, HOMO-1, LUMO, and LUMO+1 of complexes **1**-**3** in the structure determined by X-ray analysis.

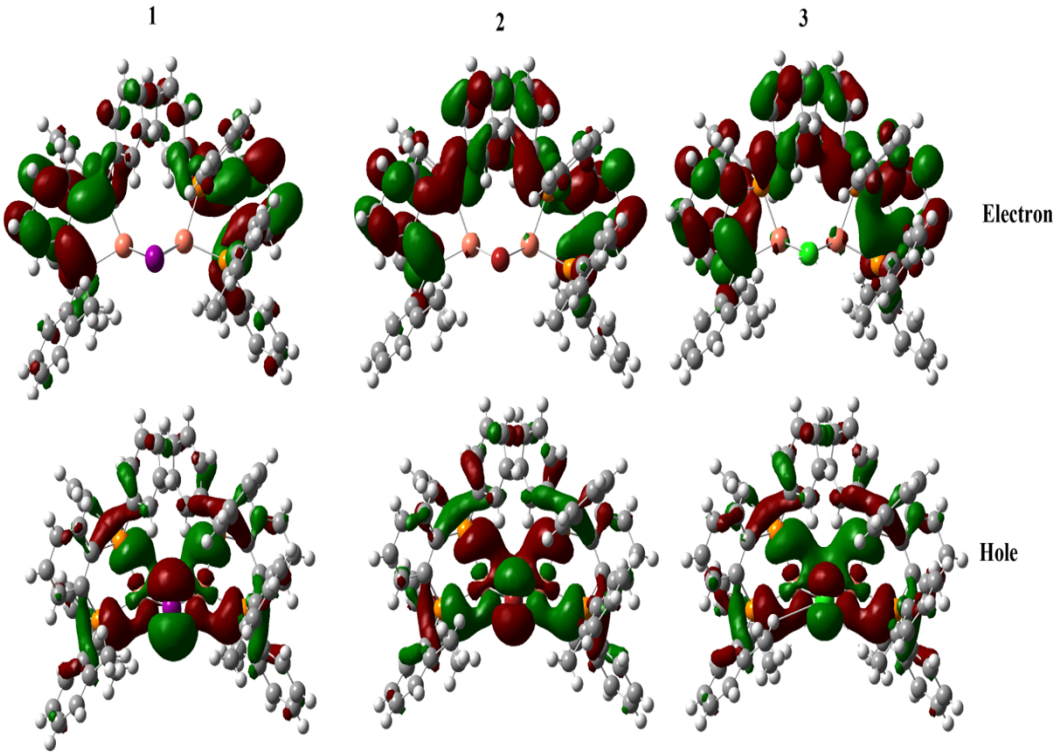

Fig. S3 Natural transition orbital pairs of the lowest triplet excited state for complexes **1**–**3** in the structure determined by X-ray analysis.

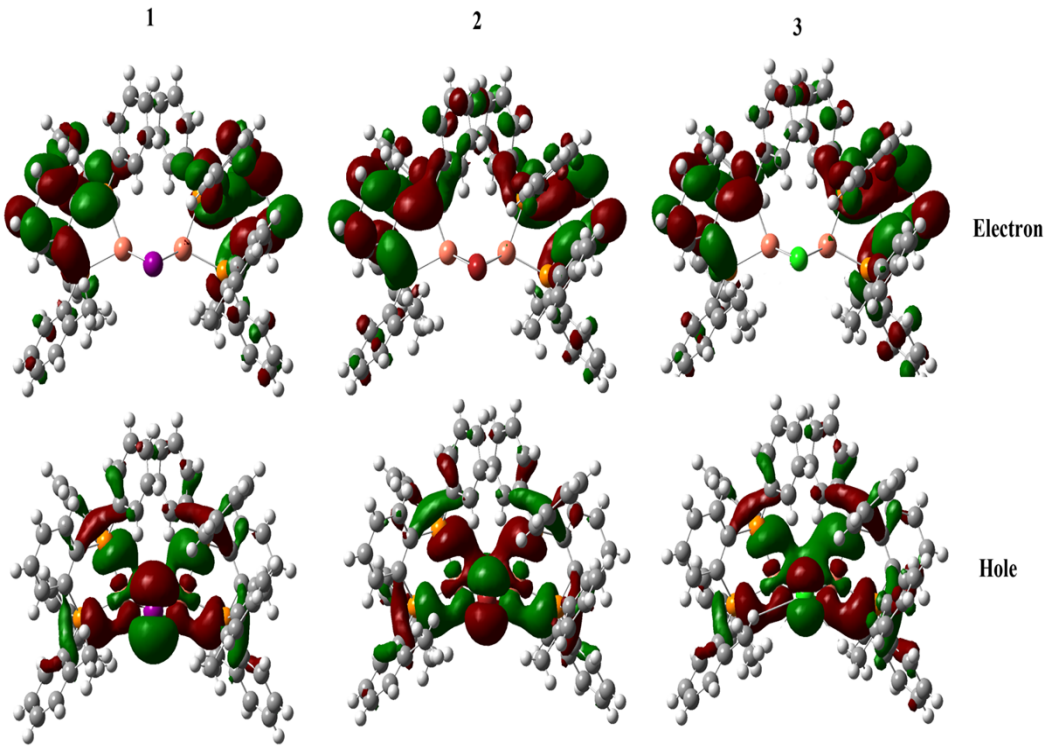

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Fig. S4 Natural transition orbital pairs of the lowest singlet excited state for complexes **1**–**3** in the structure determined by X-ray analysis.

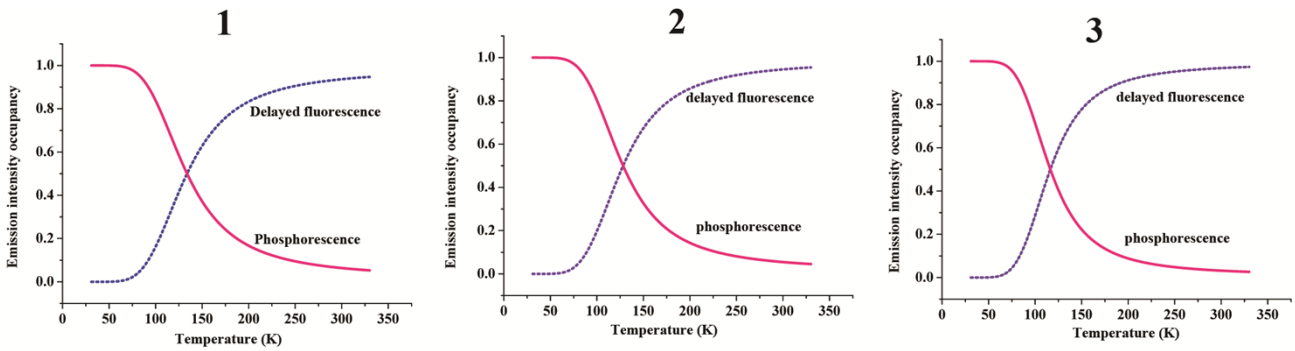

Fig. S5 The temperature-dependent emission intensity occupancies of the singlet state S1 (delayed fluorescence) and the triplet state T1 (phosphorescence) related to the total intensity for complexes **1**-**3**. The ratio of S_1 is calculated using eq. 5, and that of T_1 using $I(T_1)/(I(total) = 1- I(S_1)/(I(total)$

Temperature dependence of emissive decay times and TADF parameters fitting

Table S6 Emissive decay times (μs) at temperature from 77 to 298 K for complexes **1–3.**

Temperature/(K)	**1**	**2**	**3**
77	114.20	188.70	385.80
100	91.58	149.90	274.90
125	66.07	102.30	167.10
150	45.61	64.08	94.40
175	28.17	43.00	54.69
200	18.79	27.63	33.54
225	13.52	18.67	21.19
250	7.8021	13.90	11.1224
275	5.7804	8.3149	8.2565
298	4.9164	6.4696	6.3059