Supporting information

Circularly polarised photoluminescence and electroluminescence of chiral copper(I) dimers based on *R*/*S*-2,2'-bis(diphenyl-phosphino)-1,1'-binaphthyl ligands

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1. General information

All chemicals were used as received from commercial sources without further purification and all final products were purified by sublimation before properties investigation and application in device fabrication. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer and Bruker ARX 500 NMR spectrometer. The single crystals of complexes were carried out on a Bruker SMART CCD diffractometer using monochromated Mo Ka radiation (λ = 0.71073 Å) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections.

The absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer. The photoluminescence spectra, the absolute photoluminescence quantum yields and the decay lifetimes of the compounds were measured with HORIBA FL-3 fluorescence spectrometer. Temperature-dependent transient PL decay curve were measured with Edinburgh FLS920 fluorescence spectrometer. Thermogravimetric analysis (TGA) was performed on a Pyris 1 DSC under nitrogen at a heating rate of 10 °C min^{-1}. Cyclic voltammetry measurement was conducted on an MPI-A multifunctional

electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China), with a polished Pt plate working electrode, platinum thread counter electrode and Ag-$AgNO_3$ (0.1 M) in CH_3CN as reference electrode, *tetra*-n-butylammonium perchlorate (0.1 M) as the supporting electrolyte, using Fc^+/Fc as the internal standard and the scan rate was 0.1 V/s. The ground state geometries are based on single crystal structure, electron cloud distributions were calculated using Gaussian 09 software by density functional theory (DFT) using the B3LYP functional with the def2-SVP basis set (Ref. Gaussian 09, Revision D.01, M. J. Frisch, et al, Gaussian, Inc., Wallingford CT, 2013). The ECD spectra were measured on a Jasco J-810 circular dichroism spectrometer. CPL and CPEL spectra were performed with a JASCO CPL-300 spectrometer.

All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15 Ω/sq. The deposition rate for organic compounds is 1-2 Å/s. The phosphor and the host (2,6DCzPPy) were co-evaporated to form emitting layer from two separate sources. The cathode consisting of LiF / Al was deposited by evaporation of LiF with a deposition rate of 0.1 Å/s and then by evaporation of Al metal with a rate of 3 Å/s. The characteristic curves of the devices were measured with a computer which controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. Based on the uncorrected PL and EL spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer, The EQE of EL devices were calculated based on the photo energy measured by the photodiode.

2. NMR spectra

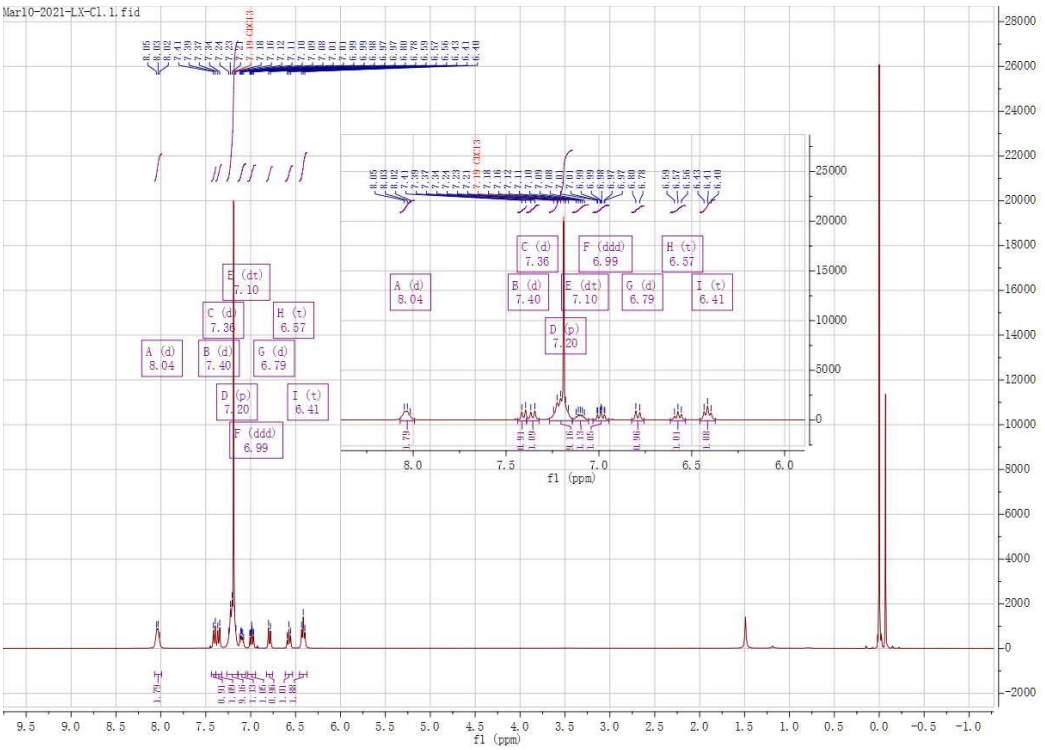

Fig. S1 ^{1}H NMR of *S*-(BINAP)$_2$Cu(μ-Cl$_2$).

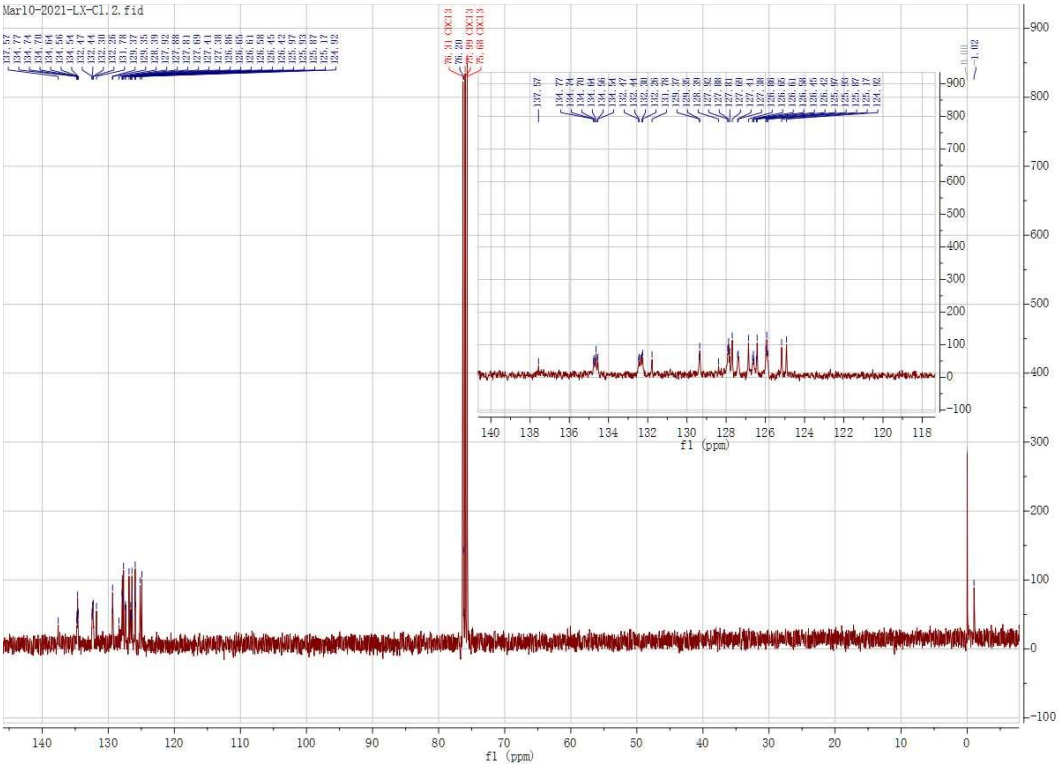

Fig. S2 ^{13}C NMR of *S*-(BINAP)$_2$Cu(μ-Cl$_2$).

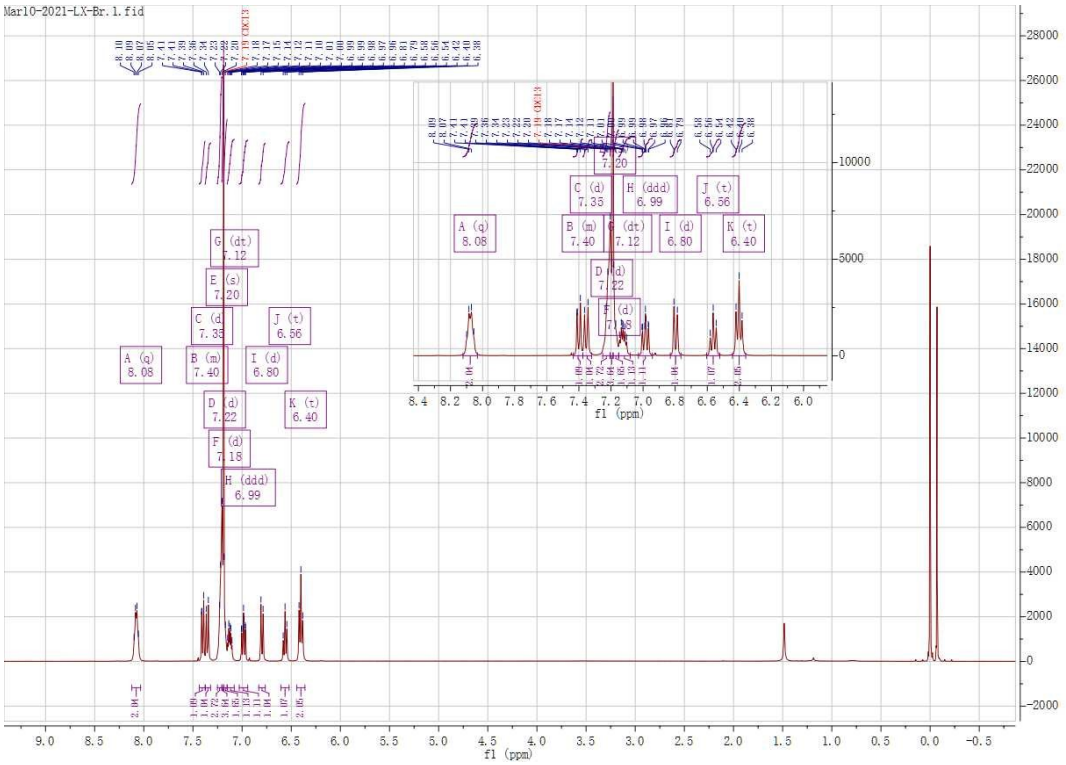

Fig. S3 ^{1}H NMR of *S*-(BINAP)$_2$Cu(μ-Br$_2$).

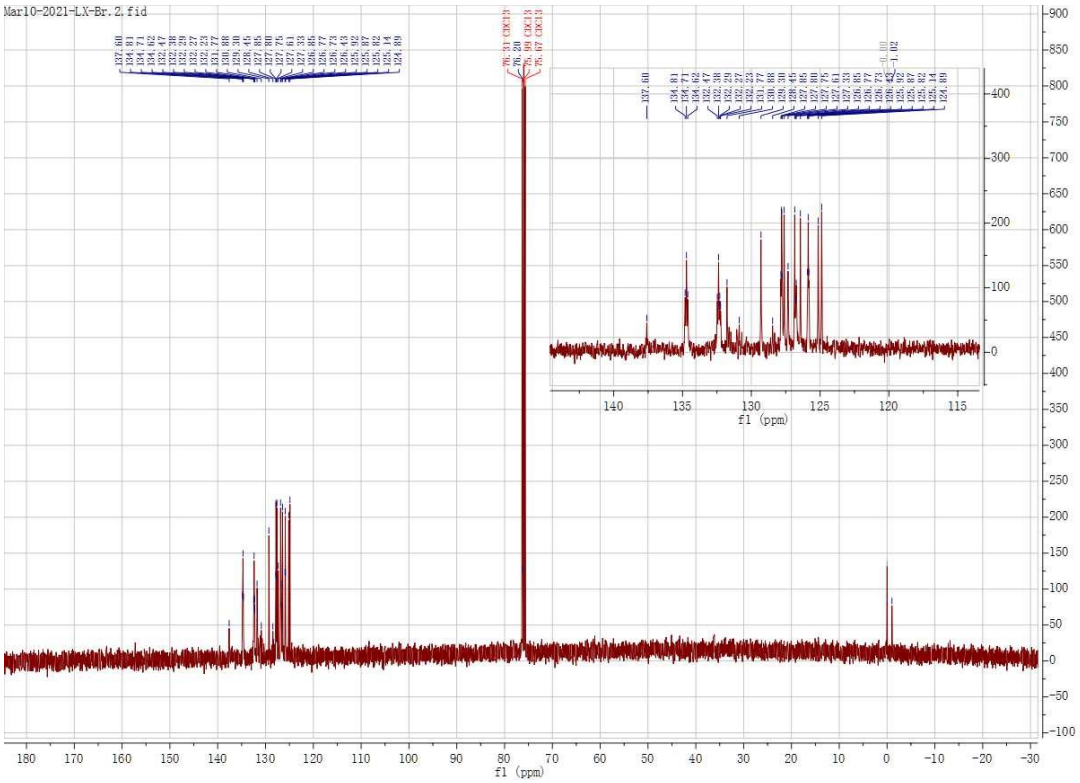

Fig. S4 ^{13}C NMR of *S*-(BINAP)$_2$Cu(μ-Br$_2$).

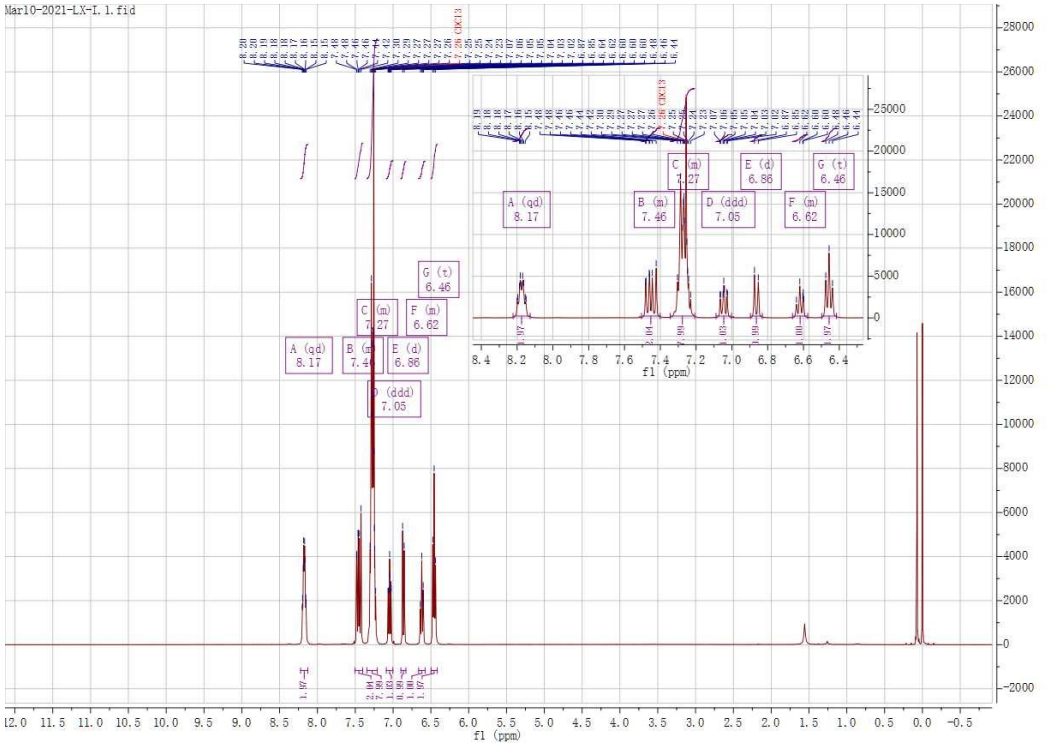

Fig. S5 ^{1}H NMR of *S*-(BINAP)$_2$Cu(μ-I$_2$).

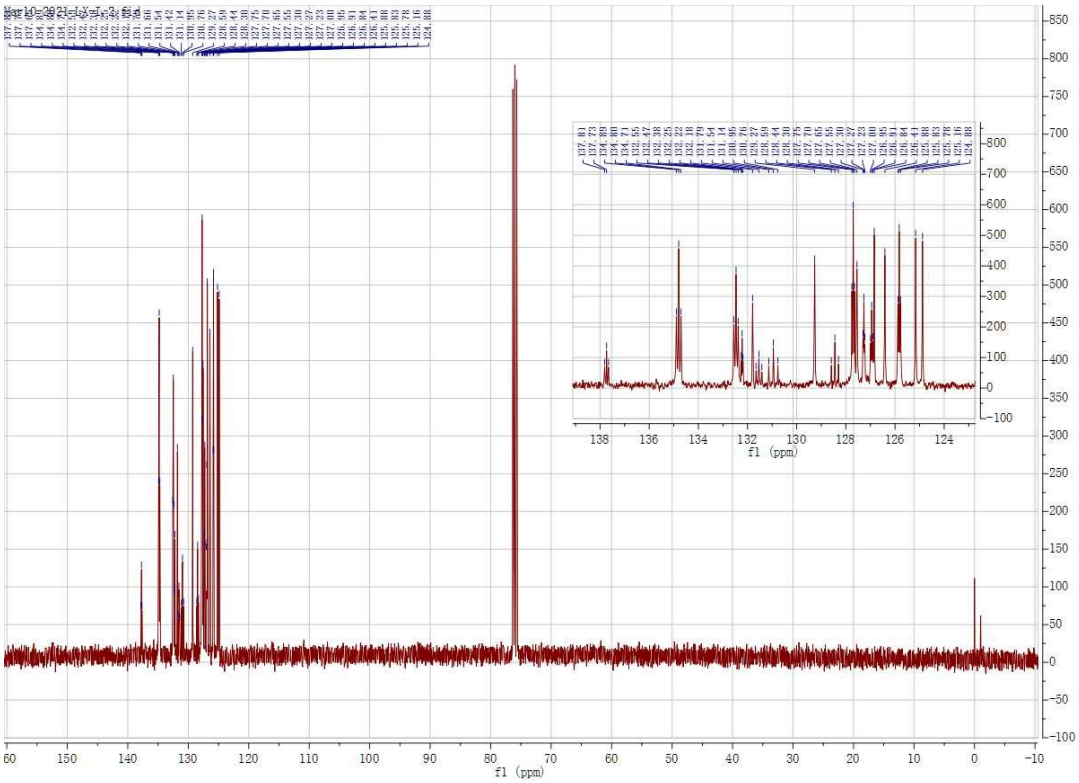

Fig. S6 ^{13}C NMR of *S*-(BINAP)$_2$Cu(μ-I$_2$).

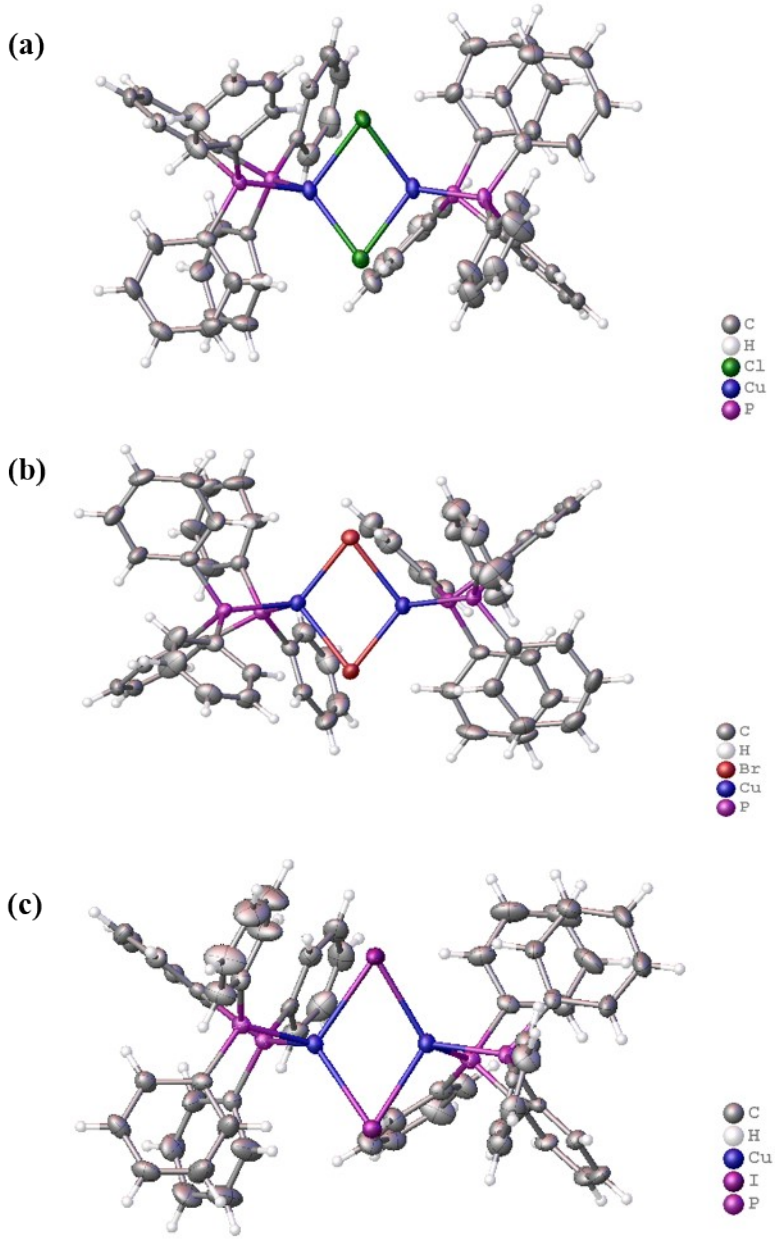

Fig. S7 Single crystal structures of (a) *S*-(BINAP)$_2$Cu(μ-Cl$_2$) (CCDC: 2068678), (b) *S*-(BINAP)$_2$Cu(μ-Br$_2$) (CCDC: 2068899) and (c) *S*-(BINAP)$_2$Cu(μ-I$_2$) (CCDC: 2068898).

Table S1. Summary of key crystal structure parameters for three Cu(I) dimers.

	S-(BINAP)$_2$Cu(μ-Cl$_2$)	*S*-(BINAP)$_2$Cu(μ-Br$_2$)	*R*-(BINAP)$_2$Cu(μ-I$_2$)	*S*-(BINAP)$_2$Cu(μ-I$_2$)
CCDC No.	2068678	2068899	2215615	2068898
Formula	$C_{88}H_{64}Cl_2Cu_2P_4$	$C_{88}H_{64}Br_2Cu_2P_4$	$C_{88}H_{64}Cu_2I_2P_4$	$C_{88}H_{64}Cu_2I_2P_4$
FW	1443.25	1532.28	1626.17	1626.17
T (K)	293	293	296	296
Wavelength (Å)	1.34139	1.34139	0.71073	0.71073

Space group	$P4_12_12(92)$	$P4_12_12(92)$	$P4_32_12$	$P4_32_12$
a (Å)	13.8956(5)	13.907(3)	14.072(2)	14.072(2)
b (Å)	13.8956(5)	13.907(3)	14.072(2)	14.072(2)
c (Å)	35.5811(13)	35.782(7)	36.532(12)	36.532(12)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	90.00	90.00	90.00	90.00
γ (deg)	90.00	90.00	90.00	90.00
V (Å^3)	6870.27	6920.41	7234(3)	7234.11
Z	4	4	4	4
ρ_{calcd} (mg/cm^3)	1.395	1.471	1.493	1.493
μ (Mo Kα) (mm^{-1})	4.624	5.065	1.576	1.576
F (000)	2976.0	3101.1	3265.3	3265.3
$Theta_{max}$	53.910	54.190	27.410	27.410

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

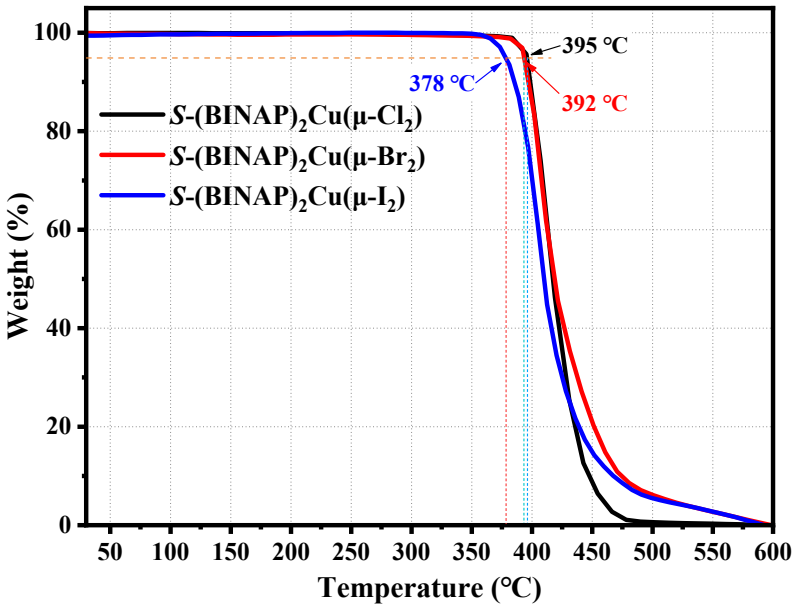

Fig. S8 TGA curves of *S*-(BINAP)$_2$Cu(μ-Cl$_2$), *S*-(BINAP)$_2$Cu(μ-Br$_2$) and *R*/*S*-(BINAP)$_2$Cu(μ-I$_2$) compounds.

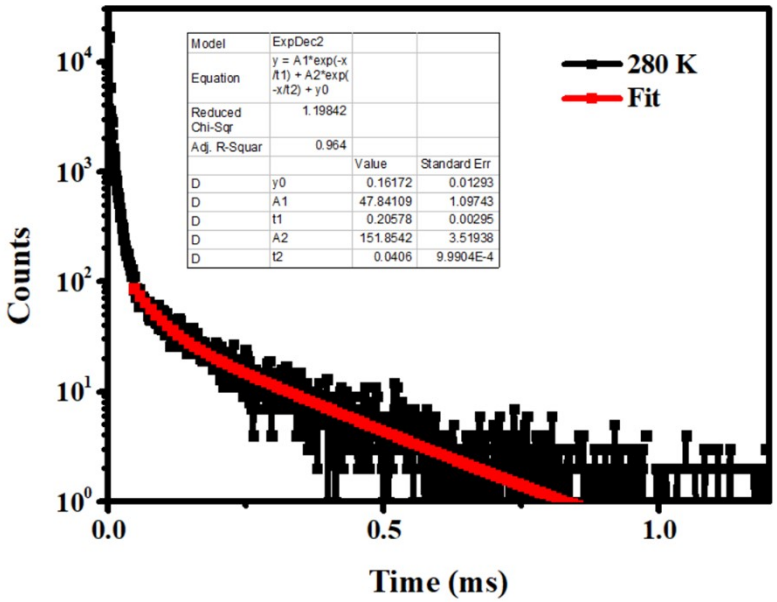

Fig. S9 Transient PL decay curve of *R*/*S*-(BINAP)$_2$Cu(μ-I$_2$) doped film in 2,6DCzppy with exponential fitting curve at 280 K.

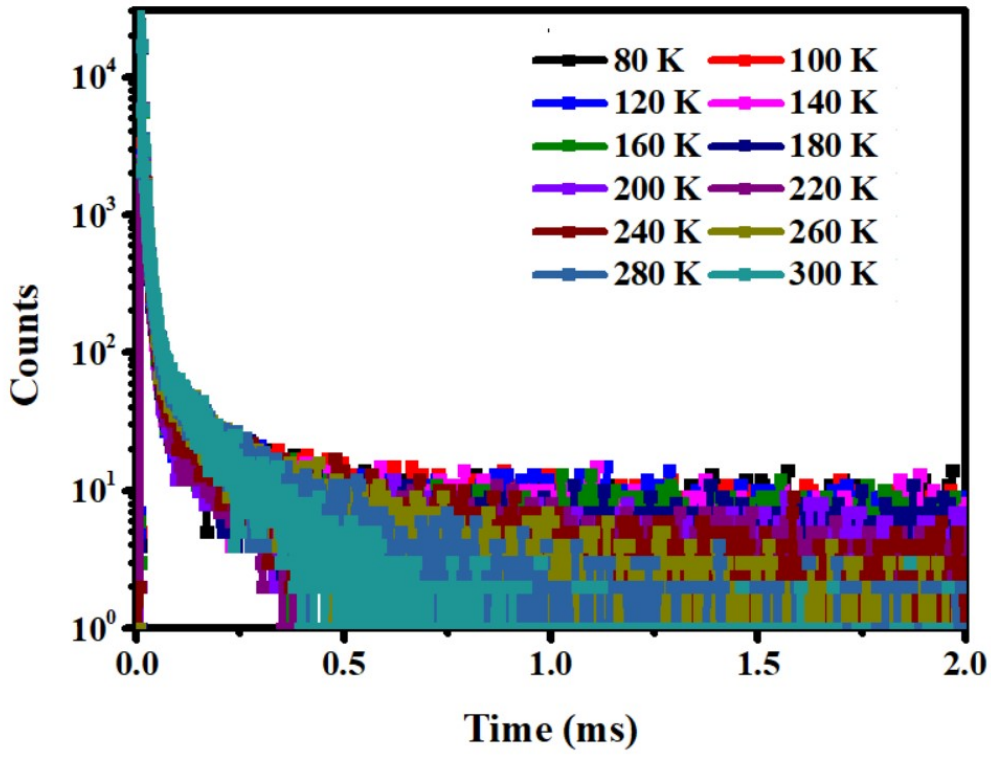

Fig. S10 Temperature-dependent transient PL decay curves of *R*/*S*-(BINAP)$_2$Cu(μ-I$_2$) doped film in 2,6DCzppy.

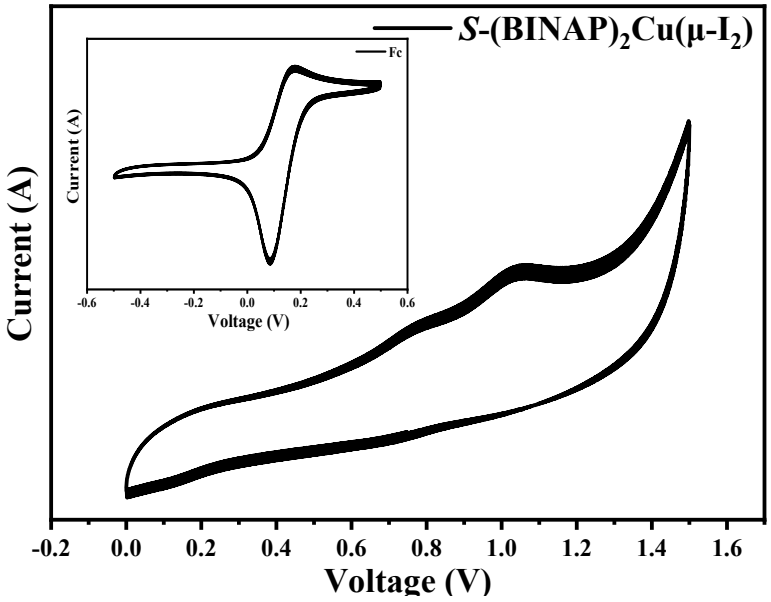

Fig. S11 Cyclic voltammetry curve of *S*-(BINAP)$_2$Cu(μ-I$_2$) dimer in acetonitrile with ferrocene as the internal standard.

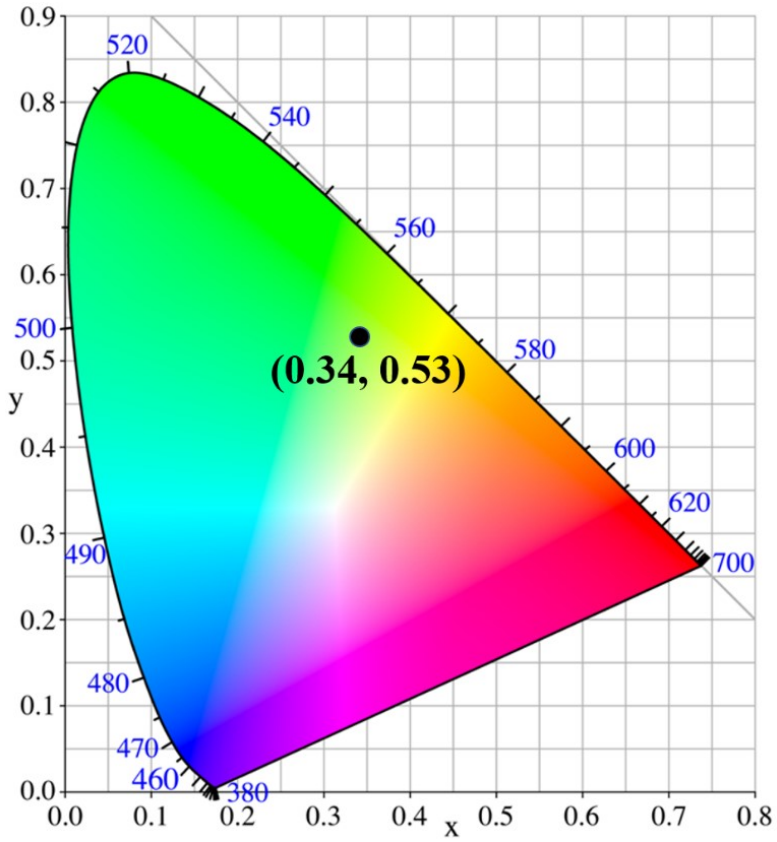

Fig. S12 CIE coordinates of device *S*-D.