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Electronic Supplementary Information

Efficiently luminescent mononuclear copper iodide complexes with sterically hindered iminephosphine chelating ligands

Bin Zhang,*[a]‡ Jie Zhang,[a]‡ Ahui Sun,[b] Chunmei Liu,[a] Mengsi Gu,[a] Yahui Chen,[a] Bin Wei,[b] Chenxia Du *[a]

[a] College of Chemistry, Zhengzhou University, Zhengzhou, 450001, P. R. China E-mail: bz@zzu.edu.cn, dcx@zzu.edu.cn

[b] Microelectronic R&D Center, School of Mechatronic Engineering and Automation, Shanghai University, Shanghai, 200072, P. R. China

‡ These authors equally contributed to the work.

Experimental section

1. General methods.

All reagents were used without further purification unless otherwise stated. Tetrahydrofuran (THF) was purified in accordance with the solvent purification manual. NMR spectra were obtained by employing a Bruker DPX-400 MHz spectrometer. Elemental analysis for C, H and N were acquired on a Carlo-Erba1106 Elemental analyzer. UV-vis spectra were recorded on a Perkin-Elmer Lambda 365 UV/vis spectrophotometer. The photoluminescence spectra and decay time were collected by an Edinburgh Analytical instrument FLS980. ARS Liquid helium cryostat is used for the temperature-dependent experiments. Electrospray ionization (ESI) mass spectra of the compounds were conducted by an Agilent 6420 instrument in CH_3OH. Photoluminescence quantum yields of the complexes in solid-state were measured through an absolute method by employing an integrating sphere.

2. X-ray Crystallography

The diffraction data for complex **1** was collected on an Oxford Xcalibur four-circle diffractometer equipped with Cu (λ = 1.54184 Å) radiation sources. The program CrysAlisPro was used for collection and reduction the data.[1] The X-ray diffraction data for the complexes **2** and **3** were collected on a Bruker D8-Venture diffractometer equipped with Mo (λ = 0.71073 Å) radiation sources.

The programs SHELXS were used to solve structures of complexes **1**-**3**,[2] and then all non-hydrogen atoms were anisotropically refined by full-matrix least-squares on F^2 using SHELXL programs[3] within Olex2 software package.[4] All hydrogen atom positions were calculated in ideal positions and refined in a riding model. CCDC 2057722-2057724 contained the supplementary crystallographic data for **1**-**3**, respectively, which could be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www. ccdc. cam. ac. uk/data_request/cif.

3. Theoretical calculations

The data of calculation were obtained by the Gaussian 09 program package.[5] The X-ray single crystal structure of copper(I) complexes were used as initial geometric structures for optimization. The geometric structures of the complexes in the ground state (S_0) were optimized by density functional theory (DFT) method with B3LYP hybrid exchange correlation functional.[6-8] Time-dependent density functional theory (TD-DFT) was used to perform the absorption transitions including vertical excitation energies and oscillator strengths. In these calculations, the "double-ζ" quality basis set (LANL2DZ) was used for heavy atoms Cu and I, and 6-31G(d, p) basis set was employed to depict other atoms (C, H, O, N and P).[9, 10] Visualization of the frontier molecular orbitals, optimized structures and simulated absorption spectra were performed by GaussView and Multiwfn 3.4.1 program, respectively.[11]

4. OLED fabrication and characterization

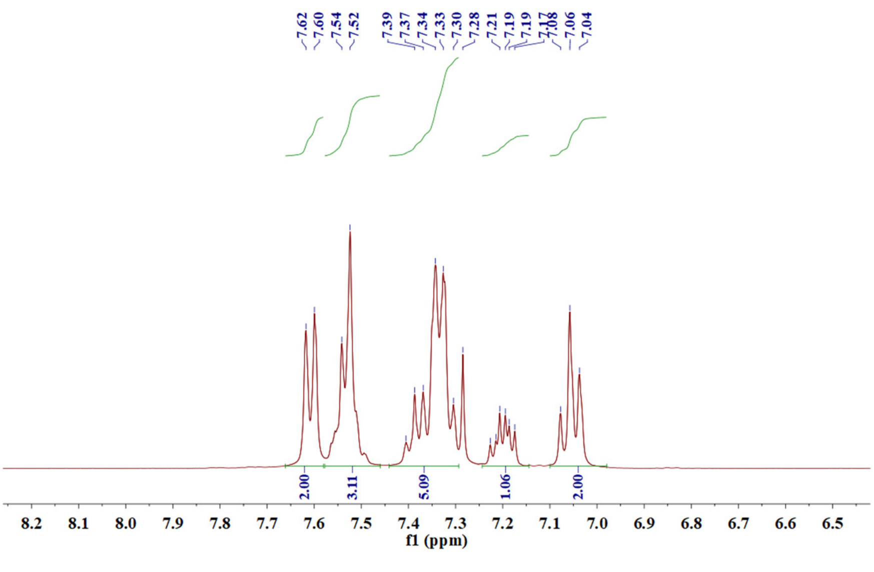
Indium-tin-oxide (ITO) coated glass substrates were cleaned before use. PEDOT:PSS film was spin-coated on top of the ITO and annealed at 120°C. After that, the emissive layer composed of 10 wt% of Cu complex and host material (mCP : TCTA = 1:1) was spin-casted onto the PEDOT:PSS layer. The layers of TmPyPb (40 nm), Liq (1 nm) and Al (100 nm) were deposited onto the substrates by thermal evaporation under high vacuum of $<3*10^{-4}$ Pa without vacuum break. Electroluminescent (EL) spectra and CIE coordinates were recorded with PR650 spectrometer. The current density (J)-voltage (V)-luminance (L) characteristics of the devices were carried out on a computer-controlled programmable Keithley 2400 source meter. All measurements were carried out at room temperature under ambient conditions.

5. Synthesis

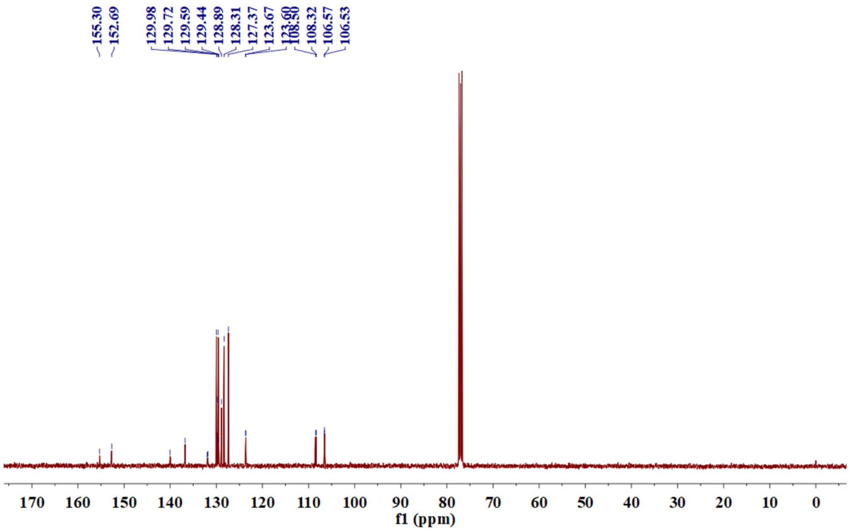
5.1. Synthesis of ligands

Synthesis of **RF1**. A mixture of **A1** (4.2 g, 18 mmol) and benzaldehyde (22 mmol) in EtOH (100 mL) and H_2O (20 mL) was stirred for 5 min. 2.5 equivalents of sodium dithionite was added to the mixture, and then the system refluxed for 5 h. After cooling down, the mixture was poured into water and extracted with ethyl acetate. The organic phase was dried with anhydrous Na_2SO_4. The solvent was removed by rotary evaporation under reduced pressure. The crude was purified by silica gel column chromatography. Yield: 76%. $C_{19}H_{13}FN_2$, FW=288.33. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66-7.58 (d, J = 7.23 Hz, 2H), 7.58-7.46 (m, 3H), 7.44-7.29 (m, 5H), 7.24-7.14 (m, 1H), 7.10-6.98 (t, J = 8.02 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.30, 152.69, 140.06, 136.78, 131.99, 131.82, 129.98, 129.72, 129.59, 129.44, 128.89, 128.31, 127.37, 123.67, 123.60, 108.50, 108.32, 106.57, 106.53. Anal. Calcd/%: C, 79.16; H, 4.51; N, 9.72. Found: C, 79.13; H, 4.53; N, 9.75.

RF1 ^1H NMR (400 MHz, $CDCl_3$)

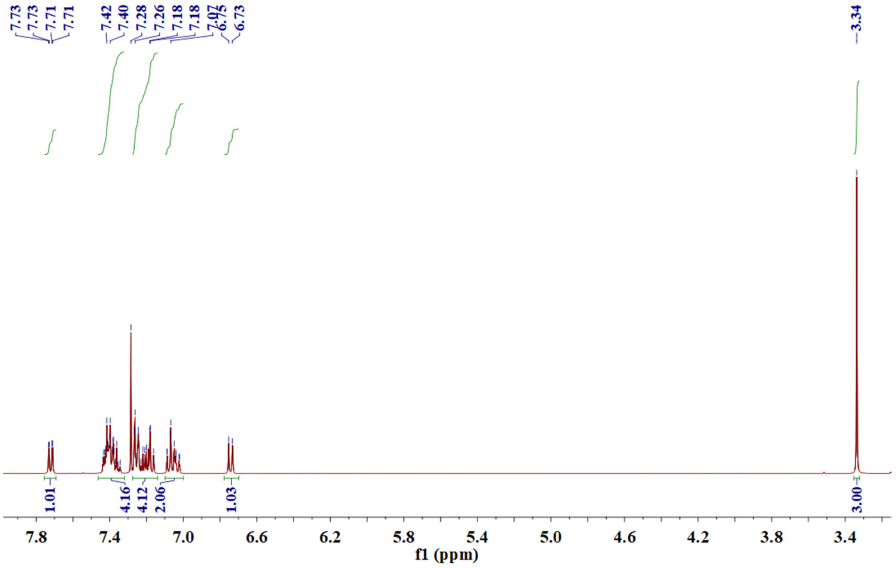


RF1 ^{13}C NMR (101 MHz, CDCl$_3$)

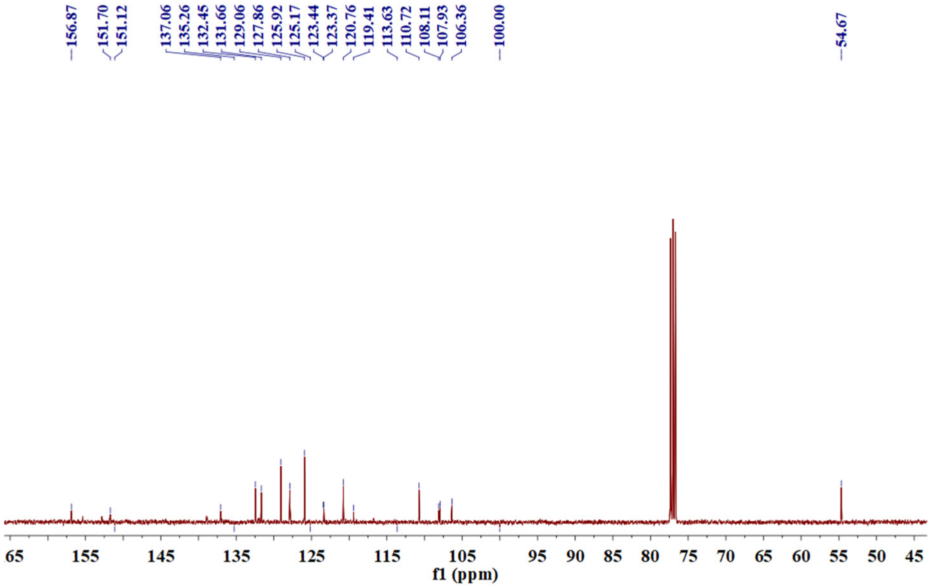


Synthesis of **RF2**. This compound was prepared by using the method similar to that described in the synthesis of **RF1**. Yield: 70%. $C_{20}H_{15}FN_2O$, FW=318.35. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76-7.69 (dd, J = 7.54, 1.72 Hz, 1H), 7.46-7.32 (m, 4H), 7.28-7.14 (m, 4H), 7.10-7.00 (m, 2H), 6.78-6.70 (d, J = 8.23 Hz, 1H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 156.87, 151.70, 151.12, 137.06, 135.26, 132.45, 131.66, 129.06, 127.86, 125.92, 125.17, 123.44, 123.37, 120.76, 119.41, 113.63, 110.72, 108.11, 107.93, 106.36, 100.00, 54.67. Anal. Calcd/%: C, 75.47; H, 4.72; N, 8.80. Found: C, 75.45; H, 4.73; N, 8.83.

RF2 ^{1}H NMR (400 MHz, CDCl$_3$)

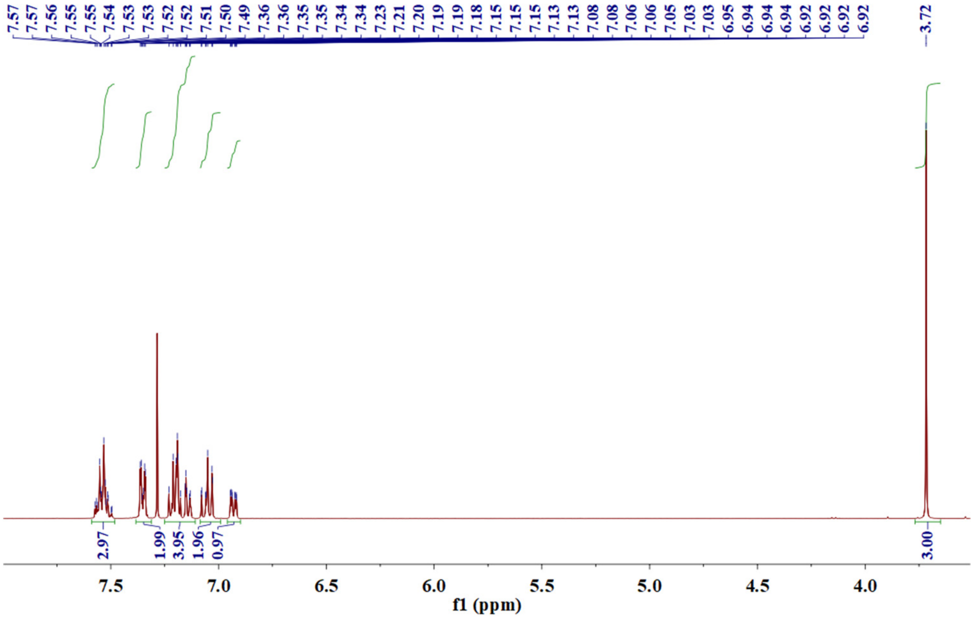


RF2 ^{13}C NMR (101 MHz, $CDCl_3$)

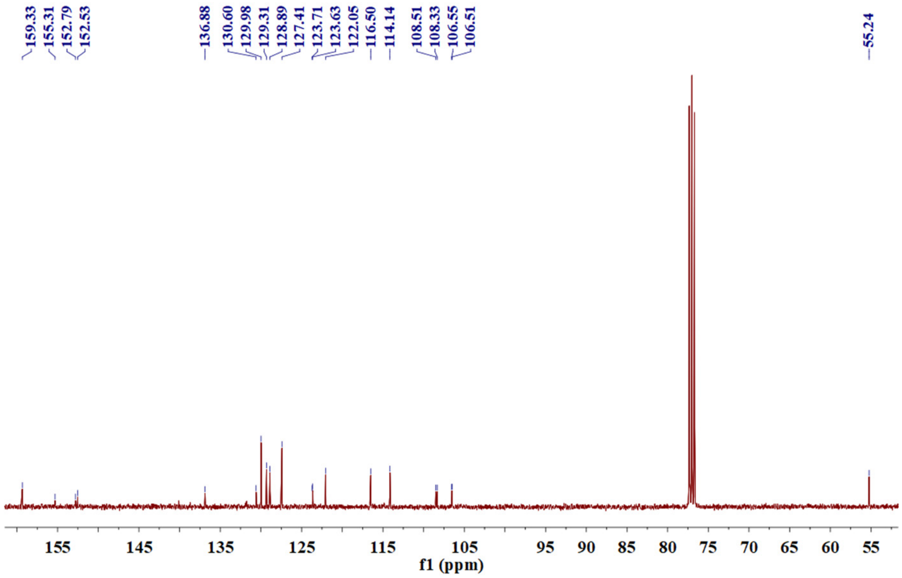


Synthesis of **RF3**. This compound was prepared by using the method similar to that described in the synthesis of **RF1**. Yield: 73%. $C_{20}H_{15}FN_2O$, FW=318.35. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59-7.48 (m, 3H), 7.38-7.31 (m, 2H), 7.25-7.11 (m, 4H), 7.09-6.99 (m, 2H), 6.96-6.90 (m, 1H), 3.72 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.33, 155.31, 152.79, 152.53, 136.88, 130.60, 129.98, 129.31, 128.89, 127.41, 123.71, 123.63, 122.05, 116.50, 114.14, 108.51, 108.33, 106.55, 106.51, 55.24. Anal. Calcd/%: C, 75.46; H, 4.72; N, 8.80. Found: C, 75.42; H, 4.73; N, 8.82.

RF3 ^1H NMR (400 MHz, $CDCl_3$)

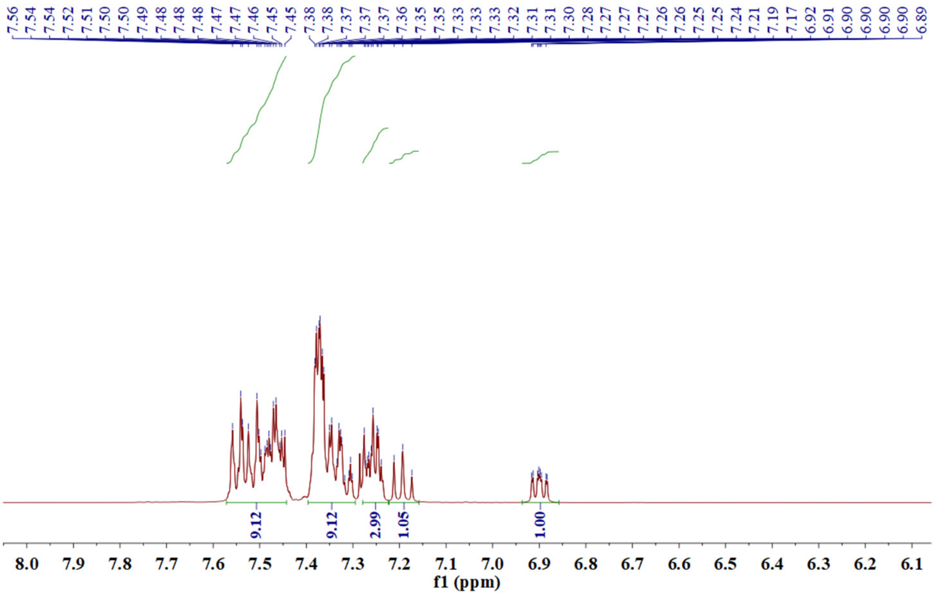


RF3 ^{13}C NMR (101 MHz, CDCl$_3$)

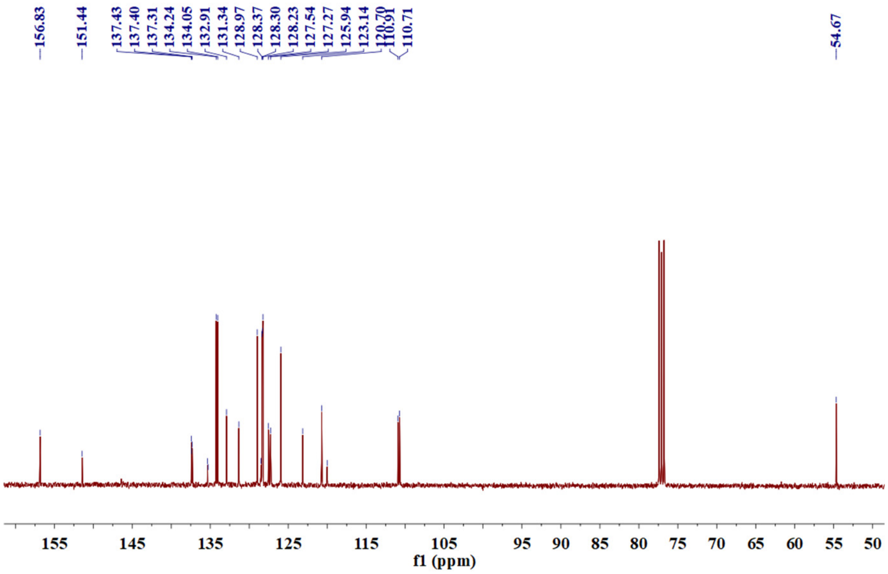


Synthesis of **L1.** Under an argon atmosphere, potassium diphenylphosphide (10.5 mmol, 0.5 M in THF) was added in dropwise to a stirred solution of **RF1** (10.0 mmol) in 22 mL anhydrous THF. After that, the mixture was refluxed overnight. The tetrahydrofuran was removed by evaporation under reduced pressure and the residue was recrystallized by 25 mL methanol. After filtration, the solid was washed with methanol and H_2O, and then dried under vacuum to obtain the ligand **L1**. Yield: 82%. $C_{31}H_{23}N_2P$, FW=454.51. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57-7.44 (m, 9H), 7.40-7.29 (m, 9H), 7.28-7.22 (m, 3H), 7.22-7.16 (t, J = 7.66, 7.66 Hz, 1H), 6.90 (m, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 156.83, 151.44, 137.43, 137.40, 137.31, 135.35, 135.29, 134.24, 134.05, 132.91, 131.34, 128.97, 128.50, 128.37, 128.30, 128.23, 127.54, 127.27, 125.94, 123.14, 120.70, 120.00, 110.91, 110.71, 54.67. ^{31}P NMR (162 MHz, CDCl$_3$) δ -18.11 (s). Anal. Calcd/%: C, 81.94; H, 5.06; N, 6.17. Found: C, 81.94; H, 5.09; N, 6.14.

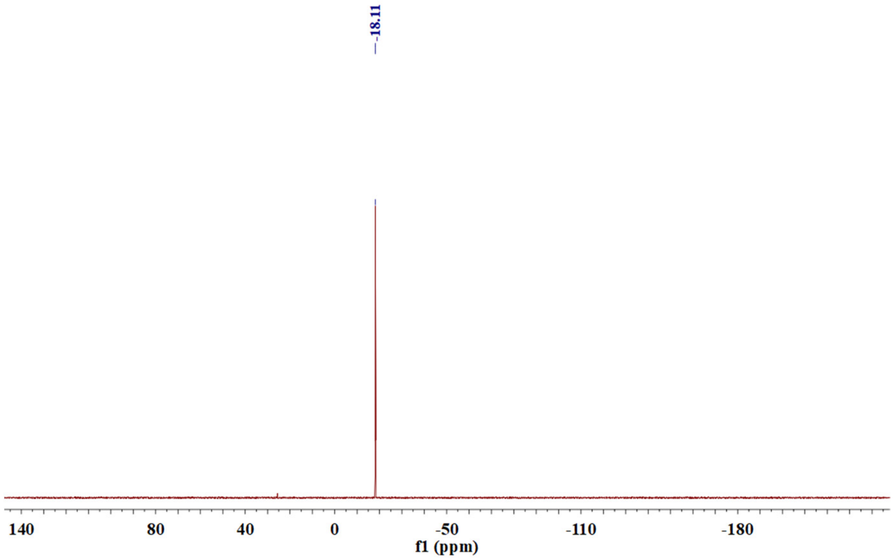
L1 ^{1}H NMR (400 MHz, CDCl$_3$)



L1 ^{13}C NMR (101 MHz, $CDCl_3$)

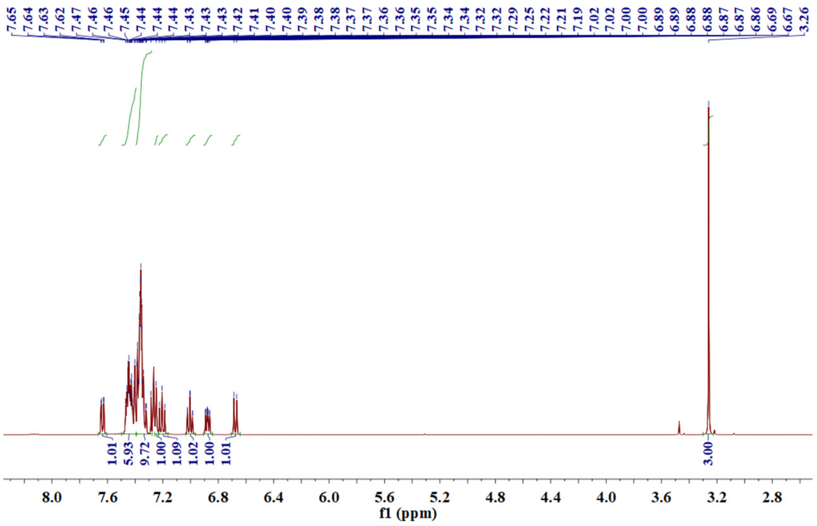


L1 ^{31}P NMR (162 MHz, $CDCl_3$)

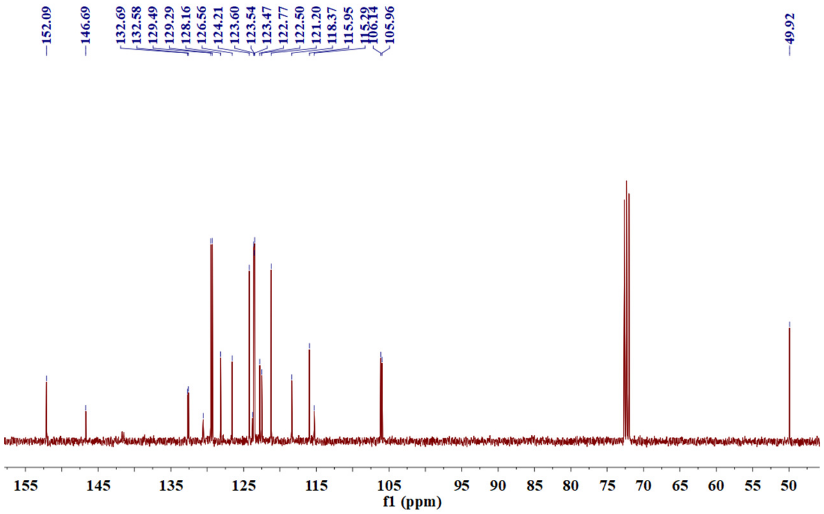


Synthesis of **L2.** This compound was prepared by using the method similar to that described in the synthesis of **L1**. Yield: 61%. $C_{32}H_{25}N_2OP$, FW=484.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.53, 1.71 Hz, 1H), 7.50-7.39 (m, 6H), 7.39-7.28 (m, 10H), 7.25 (s, 1H), 7.21 (t, J = 7.72, 7.72 Hz, 1H), 7.00 (m, 1H), 6.88 (m, 1H), 6.68 (d, J = 8.18 Hz, 1H), 3.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.09, 146.69, 132.69, 132.58, 130.55, 129.49, 129.29, 128.16, 126.56, 124.21, 123.76, 123.60, 123.54, 123.47, 122.77, 122.50, 121.20, 118.37, 115.95, 115.29, 106.14, 105.96, 49.92. ^{31}P NMR (162 MHz, $CDCl_3$) δ -18.39 (s). Anal. Calcd/%: C, 79.34; H, 5.17; N, 5.78. Found: C, 79.35; H, 5.20; N, 5.77.

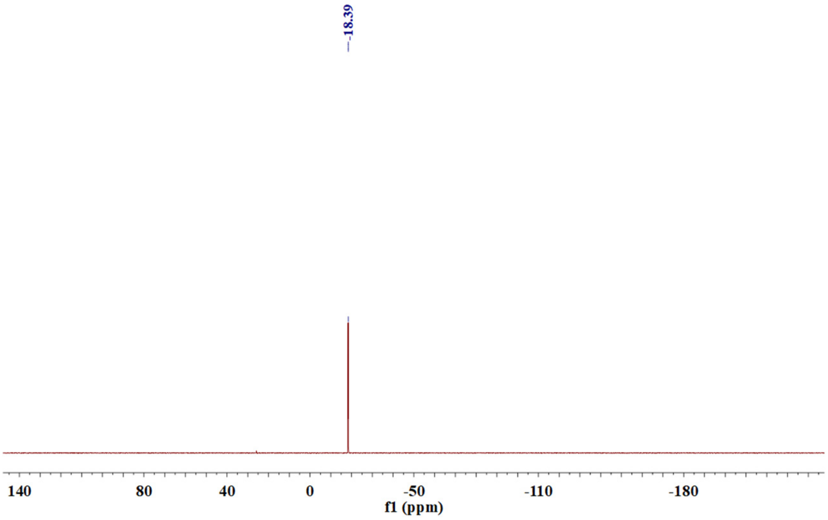
L2 ^{1}H NMR (400 MHz, $CDCl_3$)



L2 ^{13}C NMR (101 MHz, $CDCl_3$)

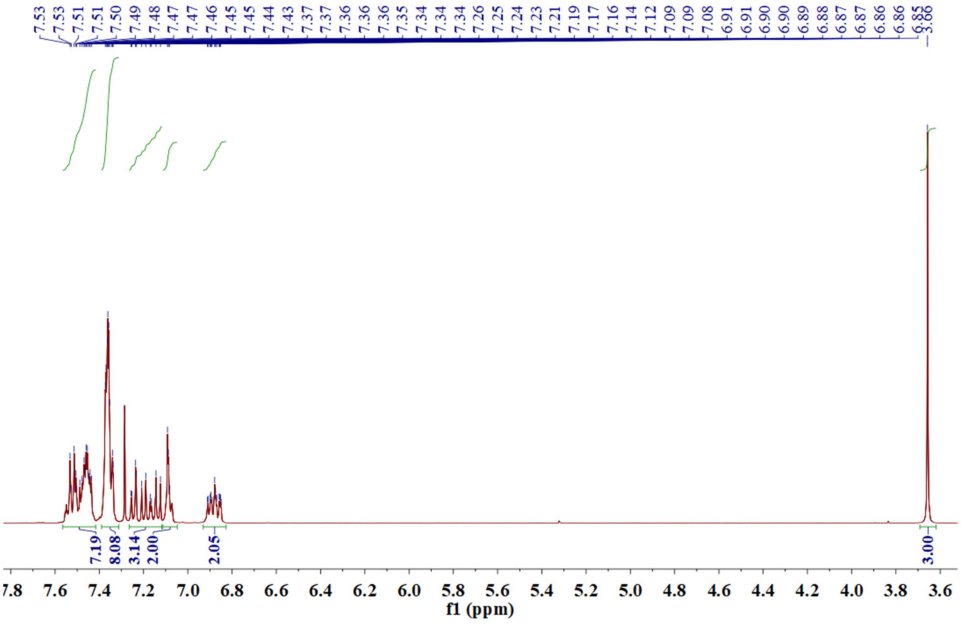


L2 ^{31}P NMR (162 MHz, $CDCl_3$)

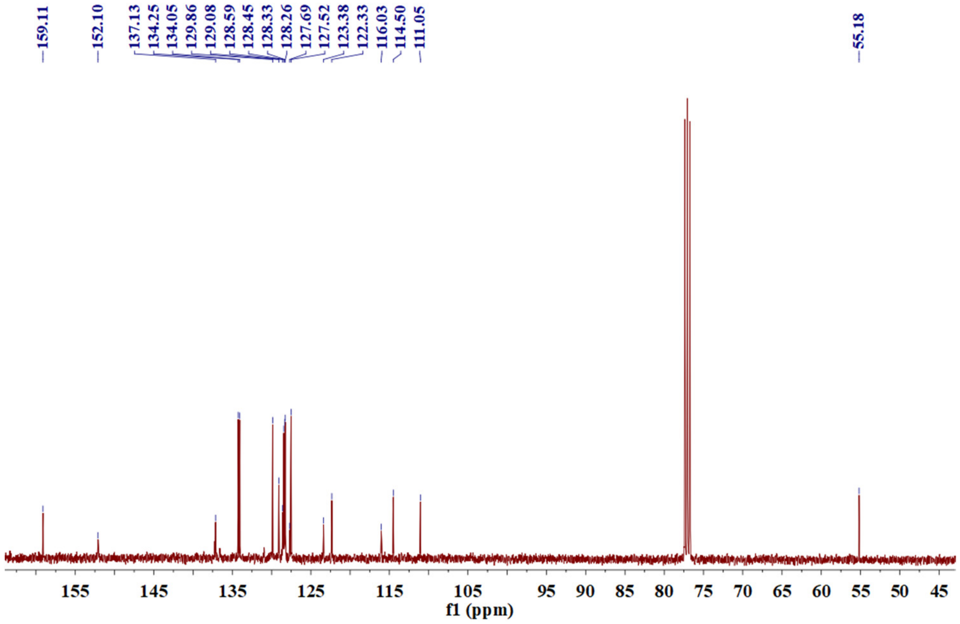


Synthesis of **L3.** This compound was prepared by using the method similar to that described in the synthesis of **L1**. Yield: 70%. $C_{32}H_{25}N_2OP$, FW=484.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.42 (m, 7H), 7.39-7.31 (m, 8H), 7.26-7.12 (m, 3H), 7.11-7.05 (m, 2H), 6.93-6.83 (m, 2H), 3.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.11, 152.10, 137.13, 134.25, 134.05, 129.86, 129.08, 128.59, 128.45, 128.33, 128.26, 127.69, 127.52, 123.38, 122.33, 116.03, 114.50, 111.05, 55.18. ^{31}P NMR (162 MHz, $CDCl_3$) δ -17.82 (s). Anal. Calcd/%: C, 79.34; H, 5.17; N, 5.78. Found: C, 79.30; H, 5.19; N, 5.75.

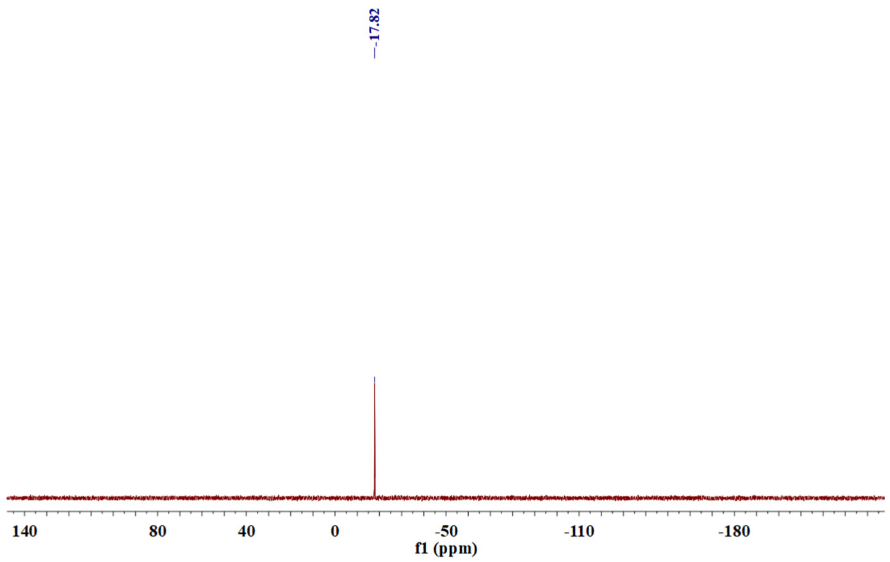
L3 ^{1}H NMR (400 MHz, $CDCl_3$)



L3 ^{13}C NMR (101 MHz, $CDCl_3$)



L3 ^{31}P NMR (162 MHz, $CDCl_3$)

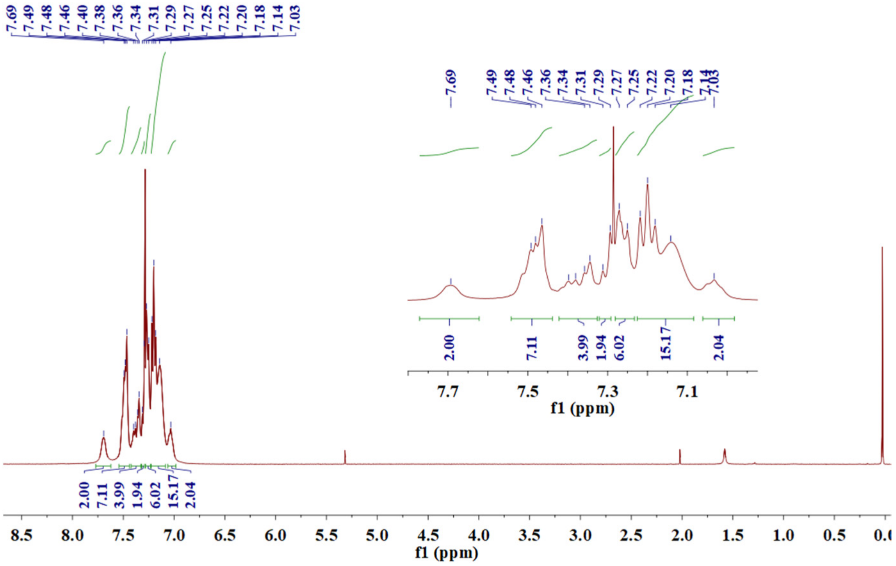


5.2. Synthesis of Cu(I) complexes

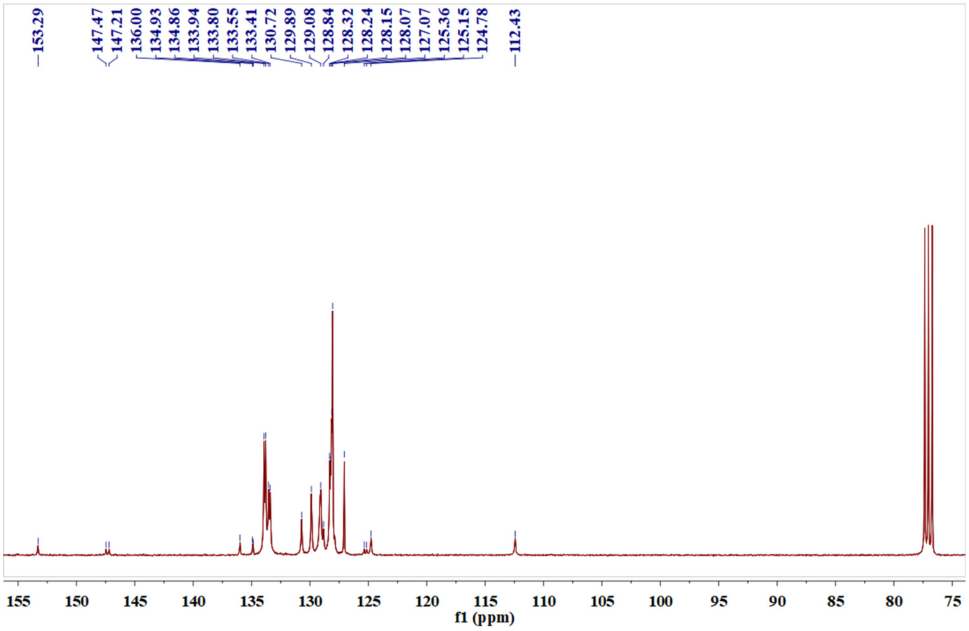
All complexes were prepared using a similar procedure (**Scheme 1**). A mixture of CuI (1 mmol), P^N ligand and PPh_3 (1 mmol) in MeCN (15 ml) was stirred for 5 h at room temperature. The mixture was filtered, and then the filtrate concentrated by slow evaporation at room temperature, which afforded crystals suitable for single crystal X-ray diffraction studies. Yields: 60-73%.

1 ($C_{49}H_{38}N_2P_2CuI$): Yield: 72%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.54-7.44 (m, 7H), 7.42-7.33 (m, 4H), 7.32-7.29 (m, 2H), 7.28-7.23 (m, 6H), 7.23-7.09 (m, 15H), 7.03 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.29, 147.47, 147.21, 136.00, 134.93, 134.86, 133.94, 133.80, 133.55, 133.41, 130.72, 129.89, 129.08, 128.84, 128.32, 128.24, 128.15, 128.07, 127.07, 125.36, 125.15, 124.78, 112.43. ^{31}P NMR (162 MHz, $CDCl_3$) δ -6.22 (s), -25.30 (s). m/z: $[M-I]^+$ calc 779.1806, found 779.1000; Anal. Calcd/ %: C, 64.83; H, 4.19; N, 3.09. Found: C, 64.85; H, 4.20; N, 3.07.

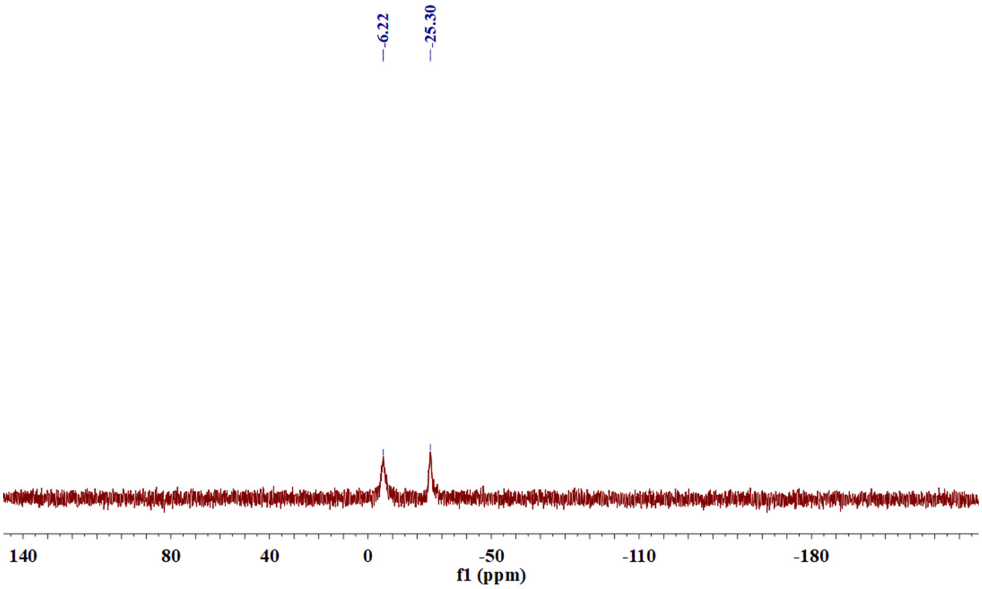
1 ^1H NMR (400 MHz, $CDCl_3$)

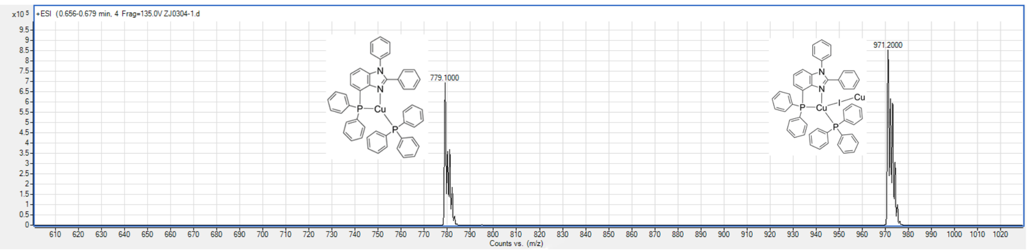


1 ^{13}C NMR (101 MHz, $CDCl_3$)



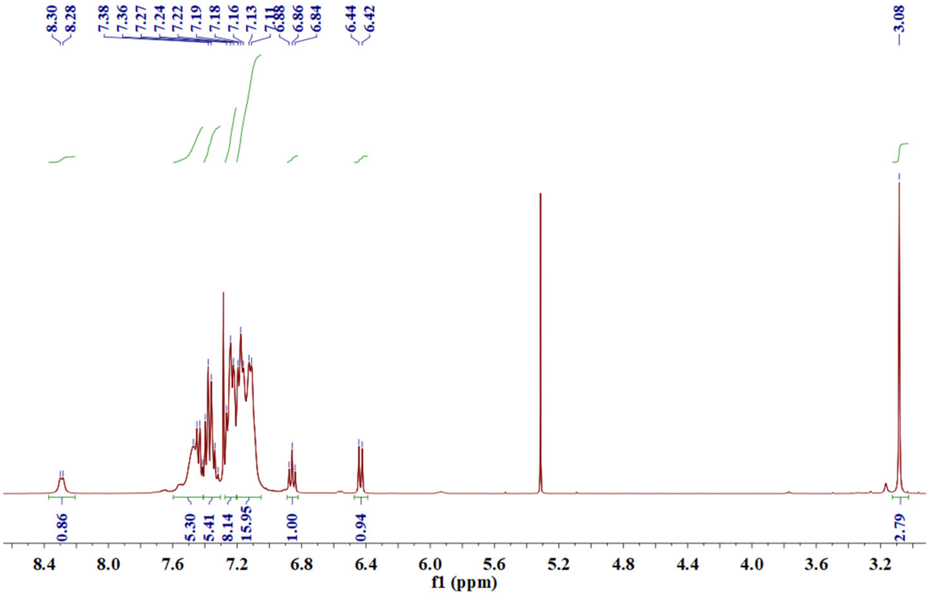
1 ^{31}P NMR (162 MHz, $CDCl_3$)



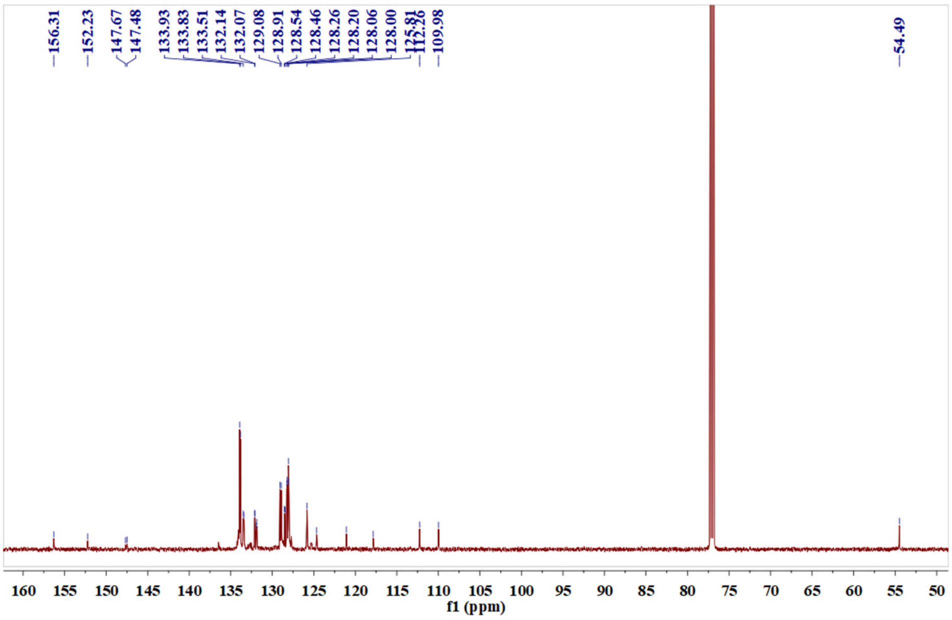


2 ($C_{50}H_{40}N_2OP_2CuI$): Yield: 60%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 6.55 Hz, 1H), 7.60-7.41 (m, 5H), 7.41-7.30 (m, 5H), 7.28-7.20 (m, 8H), 7.20-7.05 (m, 16H), 6.86 (t, J = 7.49, 7.49 Hz, 1H), 6.43 (d, J = 8.31 Hz, 1H), 5.31 (s, 1H), 3.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.31, 152.23, 147.67, 147.48, 133.93, 133.83, 133.51, 133.41, 132.14, 132.07, 131.93, 131.85, 129.08, 128.91, 128.54, 128.46, 128.26, 128.20, 128.06,128.00, 125.81, 124.65, 121.07, 117.84, 112.26, 109.98, 54.49. ^{31}P NMR (162 MHz, $CDCl_3$) δ -6.01 (s), -24.94 (s). m/z: $[M-I]^+$ calc 809.1912, found 809.1000; Anal. Calcd/%: C, 64.03; H, 4.27; N, 2.99. Found: C, 64.07; H, 4.30; N, 2.96.

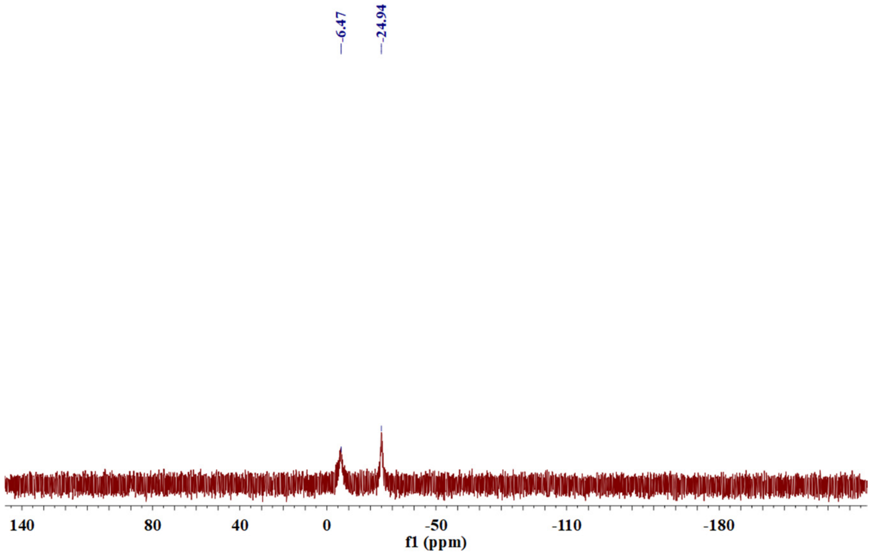
2 ^{1}H NMR (400 MHz, $CDCl_3$)

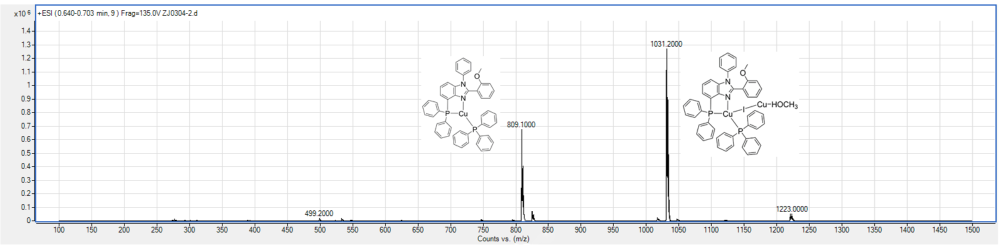


2 ^{13}C NMR (101 MHz, $CDCl_3$)



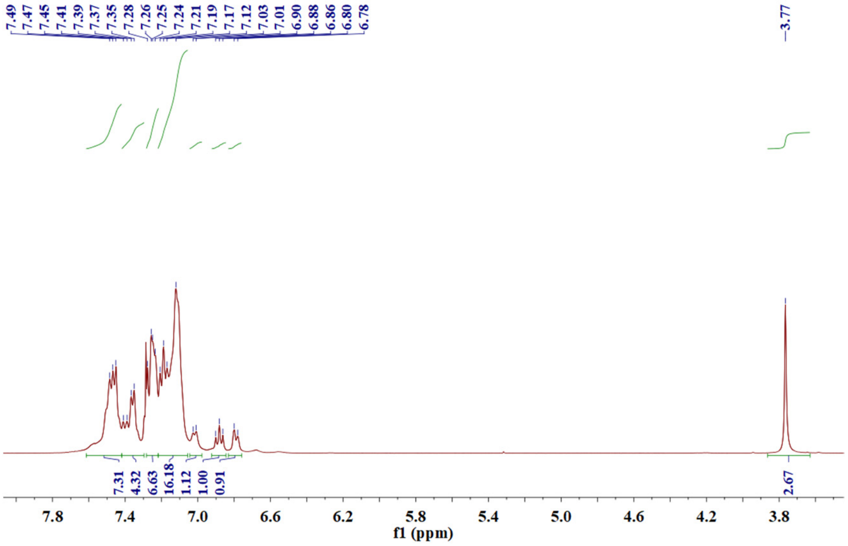
2 ^{31}P NMR (162 MHz, CDCl$_3$)



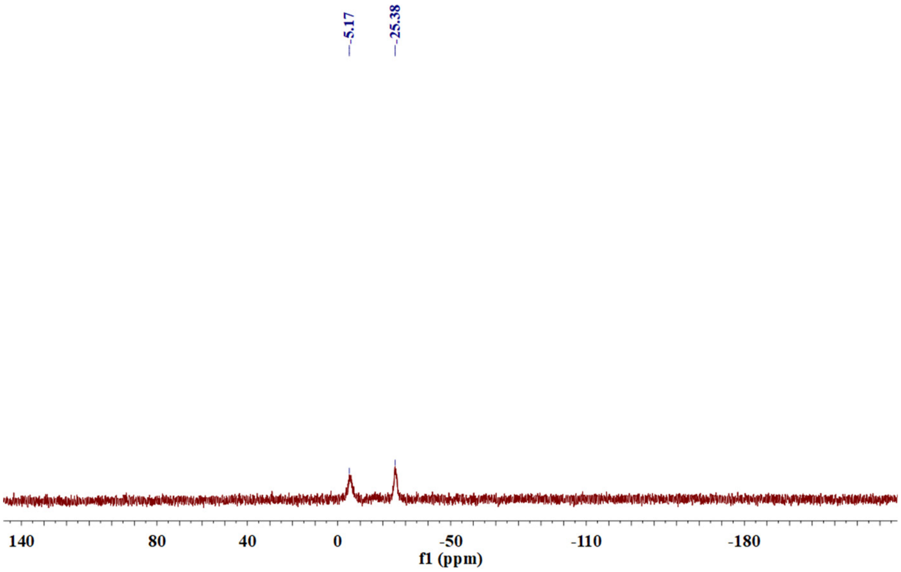


3 ($C_{50}H_{40}N_2OP_2CuI$): Yield: 73%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.62-7.42 (m, 7H), 7.42-7.30 (m, 4H), 7.28-7.22 (m, 7H), 7.22-7.05 (m, 16H), 7.02 (d, J = 6.50 Hz, 1H), 6.88 (t, J = 7.88, 7.88 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 3.77 (s, 1H). ^{31}P NMR (162 MHz, CDCl$_3$) δ -5.17 (s), -25.38 (s). m/z: [M-I]$^+$ calc 809.1912, found 809.1000; Anal. Calcd/%: C, 64.03; H, 4.27; N, 2.99. Found: C, 64.09; H, 4.29; N, 3.01.

3 ^{1}H NMR (400 MHz, CDCl$_3$)



3 ^{31}P NMR (162 MHz, CDCl$_3$)



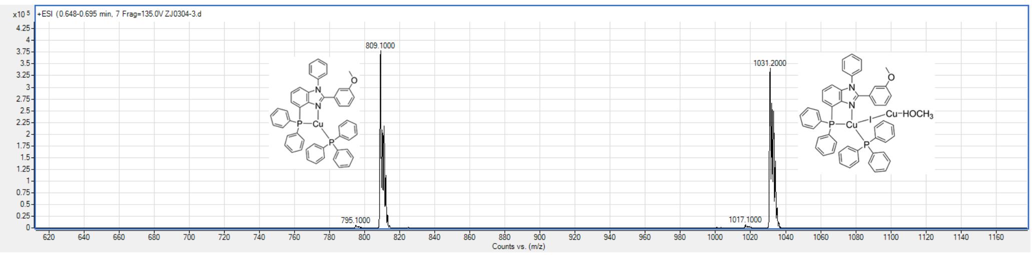


Table S1 Crystal parameters of complexes **1-3**

Compound reference	**1**	**2**	**3**
Empirical formula	$C_{49}H_{38}N_2P_2CuI$	$C_{50}H_{40}N_2OP_2CuI$	$C_{50}H_{40}N_2OP_2CuI$
Formula weight	907.19	937.22	937.22
Temperature/K	293(2)	291(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	17.6455(2)	22.454(14)	17.5705(19)
b/Å	10.80964(12)	11.131(11)	10.9974(10)
c/Å	21.9761(3)	19.860(12)	22.067(2)
α/°	90	90	90
β/°	97.1031(11)	105.914(13)	96.709(4)
γ/°	90	90	90
Volume/Å^3	4159.58(8)	4773(6)	4234.8(8)
Z	4	4	4
ρ_{calc}g/cm^3	1.449	1.304	1.470
μ/mm^{-1}	7.569	1.207	1.360
F(000)	1832.0	1896.0	1896.0
2Θ range for data collection/°	6.854 to 141.884°	4.858 to 55.052°	5.248 to 55.158°
Reflections collected	18224	102809	57438
Independent reflections	7865[R(int) = 0.0389]	10951[R(int) = 0.0415]	9751[R(int) = 0.0474]
Data/restraints/parameters	7865/0/496	10951/30/515	9751/0/515
Goodness-of-fit on F^2	1.028	1.030	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.0932	R_1 = 0.0320, wR_2 = 0.0821	R_1 = 0.0386, wR_2 = 0.1366
Final R indexes [all data]	R_1 = 0.0454, wR_2 = 0.1001	R_1 = 0.0442, wR_2 = 0.0885	R_1 = 0.0517, wR_2 = 0.1462
Largest diff. peak/hole / e Å^{-3}	0.82/-0.84	0.76/-1.00	0.44/-1.28
CCDC number	2057722	2057723	2057724

Table S2 Selected bond lengths (Å) and angles (°) for complexes **1-3**.

	1	**2**	**3**
Bond distance (Å)			
Cu1-I1	2.5738(4)	2.594(2)	2.5889(4)
Cu1-P1	2.3102(8)	2.3273(15)	2.3139(8)
Cu1-P2	2.2687(8)	2.2710(12)	2.2749(8)
Cu1-N1	2.222(2)	2.148(2)	2.230(2)
Bond angles (°)			
P1-Cu1-I1	113.19(2)	116.71(2)	114.91(2)
P2-Cu1-I1	114.99(2)	110.68(3)	114.26(2)
P2-Cu1-P1	123.69(3)	118.84(3)	122.46(3)
N1-Cu1-I1	115.22(6)	118.16(6)	116.94(6)
N1-Cu1-P1	84.66(6)	85.19(5)	84.32(6)
N1-Cu1-P2	99.52(6)	104.62(7)	98.56(6)

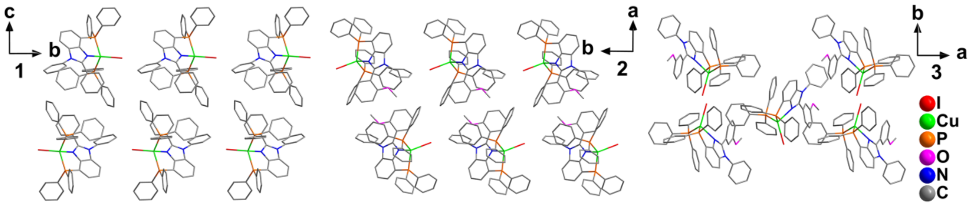


Fig. S1 Packing diagrams of the complexes. Hydrogen atoms omitted for clarity.

Table S3 Selected bond lengths (Å) and angles (°) for complexes **1-3** in ground-state.

	1	**2**	**3**
Distance (Å)			
Cu1-I1	2.6551	2.6652	2.6583
Cu1-P1	2.4634	2.4857	2.4623
Cu1-P2	2.4013	2.3865	2.3976
Cu1-N1	2.3017	2.2440	2.3023
Bond angles (°)			
P1-Cu1-I1	115.808	113.743	115.701
P2-Cu1-I1	112.955	110.912	112.734
P2-Cu1-P1	118.806	119.273	118.818
N1-Cu1-I1	121.445	117.662	121.403
N1-Cu1-P1	80.829	81.968	80.899
N1-Cu1-P2	103.048	110.749	103.501

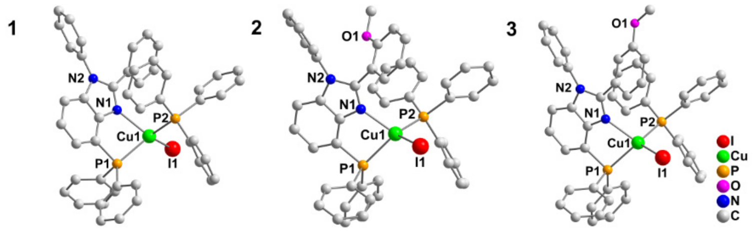


Fig. S2 The optimized structures of the complexes in the ground-state. Hydrogen atoms are omitted for clarity.

Table S4 The absorption data for the complexes **1-3**.

Compound	λ_{abs}(nm) / ε(10^4L•mol^{-1}•cm^{-1})
L1	230 / 4.54，307 / 3.13
L2	230 / 4.11，299 / 2.51
L3	230 / 4.49，307 / 2.51
1	231 / 6.47，307 / 2.76
2	230 / 6.11，301 / 2.50
3	230 / 6.52，309 / 2.66
PPh_3	229 / 3.02，266 / 1.98

Table S5 Calculated electronic transitions at the low energy band (λ > 350 nm) for complexes **1-3**.

Complex	λ_{abs} /nm	Oscillator strengths (f)	Contribution / %[a]	Transition[b]
1	373.85	0.0105	HOMO-1→LUMO (18.9) HOMO→LUMO (78.4)	(M+X)LCT
	369.69	0.0044	HOMO-1→LUMO (77.8) HOMO→LUMO (20.1)	(M+X)LCT
2	357.00	0.0103	HOMO-1→LUMO (17.6) HOMO→LUMO (81.1)	(M+X)LCT
3	373.55	0.0125	HOMO-1→LUMO (17.4) HOMO→LUMO (80.1)	(M+X)LCT
	371.53	0.0034	HOMO-1→LUMO (79.0) HOMO→LUMO (18.5)	(M+X)LCT

[a] Contribution > 15%. [b] L = N^P ligand, X = iodide

Table S6 Decay time for complexes **1-3**.

1			**2**			**3**		
T (K)	λ_{em} (nm)	τ (μs)	T (K)	λ_{em} (nm)	τ (μs)	T (K)	λ_{em} (nm)	τ (μs)
20	582	9.5	20	588	12.7	20	565	7.3
80	-	-	80	585	11.0	80	-	-
110	582	8.2	110	586	8.6	110	568	7.2
140	-	-	140	585	9.8	140	-	-
290	586	5.8	290	589	10.6	290	568	4.5
310	586	5.6	310	589	10.3	310	566	4.2

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