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Electronic Supplementary Information

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

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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 CH₃OH. 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 ($\lambda = 1.54184$ 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 ($\lambda = 0.71073$ 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 F² using SHELXL programs³ 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 spincoated 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 H₂O (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 Na₂SO₄. The solvent was removed by rotary evaporation under reduced pressure. The crude was purified by silica gel column chromatography. Yield: 76%. C₁₉H₁₃FN₂, FW=288.33. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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, CDCl₃)







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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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.







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, CDCl₃) 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).¹³C NMR (101 MHz, CDCl₃) 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.





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 H₂O, and then dried under vacuum to obtain the ligand **L1**. Yield: 82%. C₃₁H₂₃N₂P, FW=454.51. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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. ³¹P NMR (162 MHz, CDCl₃) 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 ¹H NMR (400 MHz, CDCl₃)

77.55 77





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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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. ³¹P NMR (162 MHz, CDCl₃) 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.





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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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. ³¹P NMR (162 MHz, CDCl₃) 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 ¹H NMR (400 MHz, CDCl₃)





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 (C₄₉H₃₈N₂P₂CuI): Yield: 72%. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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. ³¹P NMR (162 MHz, CDCl₃) 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.





2 (C₅₀H₄₀N₂OP₂CuI): Yield: 60%.¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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. ³¹P NMR (162 MHz, CDCl₃) 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.





3 (C₅₀H₄₀N₂OP₂CuI): Yield: 73%. ¹H NMR (400 MHz, CDCl₃) 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). ³¹P NMR (162 MHz, CDCl₃) 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.







Compound reference	1	2	3	
Empirical formula	$C_{49}H_{38}N_2P_2CuI$	C ₅₀ H ₄₀ N ₂ OP ₂ CuI	C ₅₀ H ₄₀ N ₂ OP ₂ CuI	
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)	
Ζ	4	4	4	
$\rho_{calc}g/cm^3$	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	
\mathbf{F} is the set $[\mathbf{I} > 0]$ (1)]	$R_1 = 0.0376,$	$R_1 = 0.0320,$	$R_1 = 0.0386$,	
Final K indexes $[1 \ge 2\sigma(1)]$	$wR_2 = 0.0932$	$wR_2 = 0.0821$	$wR_2 = 0.1366$	
Final R indexes [all data]	$R_1 = 0.0454,$	$R_1 = 0.0442,$	$R_1 = 0.0517,$	
r mar is mucses [an uata]	$wR_2 = 0.1001$	$wR_2 = 0.0885$	$wR_2 = 0.1462$	
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 S1 Crystal parameters of 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 an	ngles (°)				
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)			

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



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

	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		
	Во	ond 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		

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



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

Compound	$\lambda_{abs}(nm) / \epsilon(10^4 L \bullet mol^{-1} \bullet cm^{-1})$			
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 S4 The absorption data for the complexes 1-3.

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

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

^{*a*} Contribution > 15%. ^{*b*} L = N^P ligand, X = iodide

Table S6 Decay 1	time f	for comp	olexes	1-3.
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	1	1 2		3				
T (K)	$\lambda_{em}\left(nm\right)$	τ (μs)	T (K)	$\lambda_{em} (nm)$	τ (μs)	T (K)	$\lambda_{em}\left(nm\right)$	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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