Structural and Photophysical Study of Copper Iodide Complex with P^N or P^N^P Ligand

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Structural and Photophysical Study of Copper Iodide Complex with P^N or P^N^P Ligand†

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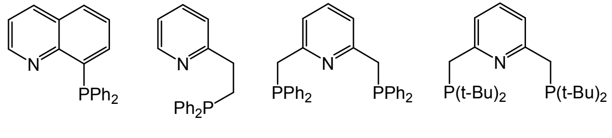
Two P^N type ligands 8-(diphenylphosphino)quinoline (**L$_1$**) and 2-[2-(diphenylphosphino)ethyl]pyridine (**L$_2$**), and two P^N^P type ligands 2,6-bis((diphenylphosphino)methyl)pyridine (**L$_3$**) and 2,6-bis((di-tert-butylphosphino)methyl)pyridine (**L$_4$**) were synthesized to coordinate with copper iodide (CuI). As a result, CuI complexes with rich structures, such as discrete complexes with formula of $[Cu_2I_2(L_1)_2]$ (**5**), $[Cu_3I_3(L_2)_2]$ (**6**), $[CuI(L_3)]$ (**7**), and polymeric complexes with repeating units of $[Cu_2I_2(L_4)]$ (**8**), $[Cu_3I_3(L_4)]$ (**9**) were synthesized and characterized by single crystal X-ray diffraction. Besides the intriguing structures, these complexes showed rich photoluminescent properties, with emission colour varied from blue to red and photoluminescence quantum yield (PLQY) from 1.6 to 29.9 % in solid state. Molecular orbital calculation and experimental study showed that the emissions involve halide to ligand charge transfer (XLCT), metal to ligand charge transfer (MLCT), and/or cluster-centered (CC) excited states.

Introduction

Luminescent materials have received increasing attention, particularly in view of their potential applications in solar energy conversion,[1,2] luminescence-based sensors,[3,4] organic light emitting diodes (OLEDs),[5-8] and biological systems[9-11]. On the basis of their applications, the synthesis and study of inexpensive, abundant luminescent Cu(I) complexes become more important. The largest class of luminescent Cu(I) complexes investigated to date is that of $[Cu(N^{\wedge}N)_2]^+$, where N^N indicates a chelating bisimine ligand, typically a substituted 1,10-phenanthroline. Study on these complexes show that luminescence originates from metal to ligand charge transfer (MLCT) excited state, which is critical to the rigidity of the ligand.[12-15] Thereafter, attention has been paid to heteroleptic $[Cu(N^{\wedge}N)(P^{\wedge}P)]^+$ complexes, where P^P denotes a bisphosphine ligand, because they exhibit greatly enhanced emission performance. For example, photoluminescence quantum yield (PLQY) close to 30% for $[Cu(POP)(dmdpp)]^+$ (POP = bis[2-(diphenylphosphino)phenyl]ether, dmdpp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) was reported, which is much higher than 1% for $[Cu(dmp)(tbp)]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline; tbp = 2,9-di-tert-butyl-1,10-phenanthroline).[16,17] Besides the structural rigidity, this is also explained as that the heteroleptic complex has higher energy MLCT excite state, which disfavors non-radiative deactivations.[15] Recently, a class of complexes with formula of [Cu(P^N)(P^P)], where P^N means a amidophosphine derivative, was found to be more promising, with high PLQY up to 70% and tunable emission colour from red to green.[18,19]

In addition to monomeric complexes, several multimeric Cu(I) complexes, especially with halide as chelator, have been reported with strong emission.[20-24] Among them, the formulated $[Cu_4I_4L_4]$ (where L is pyridine or substituted pyridine) clusters are known to be highly luminescent, and usually show two emission bands termed as high energy (HE) and low energy (LE), which sharply change their relative intensities upon temperature variation, leading to luminescent thermochromism.[24] Based on density function theory (DFT) calculation and experimental investigation, the excited states are assigned to halide to ligand charge transfer (XLCT) for the HE band, mixed halide to metal charge transfer (XMCT) and cluster centered (CC) for the LE band, respectively.[14,24,25] It is also notable that a number of Cu(I) halide complexes with planar diamond $\{Cu_2(\mu\text{-}X)_2\}$ (X = Br, I) units have been reported. By varying the N-heteroaromatic ligands, the emissions tuned from red to blue, and were assigned to MLCT excited state with some mixing of XLCT excited state.[26]



L$_1$ **L$_2$** **L$_3$** **L$_4$**

Scheme 1 Chemical structure of ligands **L$_1$-L$_4$** used to coordinate with CuI in this study.

To date, a number of Cu(I) halide complexes have been reported with isolated P- and N- ligands,[25-27] N^N ligands,[28] P^P ligands,[8,29] S ligands,[30] and so forth, while there has been few investigation of Cu(I) halide complex with P^N or P^N^P ligand, especially in view of photophysical property.[31-34]

Herein, we report on the structural and photophysical properties of five CuI complexes [$Cu_2I_2(L_1)_2$] (**5**), [$Cu_3I_3(L_2)_2$] (**6**), [CuI(L_3)] (**7**), [$Cu_2I_2(L_4)$] (**8**), and [$Cu_3I_3(L_4)$] (**9**) those derived from two P^N ligands 8-(diphenylphosphino)quinoline (**L$_1$**) and 2-[2-(diphenylphosphino)ethyl]pyridine (**L$_2$**), and two P^N^P ligands 2,6-bis((diphenylphosphino)methyl)pyridine (**L$_3$**) and 2,6-bis((di-tert-butylphosphino)methyl)pyridine (**L$_4$**) (Scheme 1), respectively.

Experimental

Instruments and Measurements:

^{1}H-NMR spectra were recorded on a Varian-400MR NMR spectrometer. Chemical shift data for each signal were reported in ppm units with $CDCl_3$ as reference, where δ ($CDCl_3$) = 7.26. Elemental analyses were performed on a Model CE 440 CHN Analyser. The photoluminescence spectra were measured by a PTI Quanta Master model C-60SE spectrophotometer, equipped with a 928 PMT detector and corrected for detector response. Phosphorescent lifetimes at room temperature were measured by time-correlated single-photon counting using an IBH Fluorocube instrument equipped with a 405 nm LED excitation source, while the lifetimes at 77 K with longer range were measured on the PTI fluorimeter equipped with a microsecond Xe flash lamp. Quantum yield measurements of both solid and solution samples were carried out using a Hamamatsu C9920 system equipped with a xenon lamp, calibrated integrating sphere and model C10027 photonic multichannel analyser.

X-ray Crystallography

Suitable single crystals for X-ray measurement of the complexes **5**-**9** were obtained as described in the preparation section. The crystals were mounted on a glass fiber with Paratone-N oil. X-ray diffraction data were collected on a Bruker SMART APEX diffractometer using graphite-monochromated Mo Kα radiation, and structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. In some cases, Patterson maps were used in place of the direct methods procedure. Detailed crystal parameters and structure refinements of the complexes **5**-**9** are given in Table 1.

Table 1 Summary of X-ray data collection and refinement of the complexes **5**-**9**

	5	**6**	**7**	**8**	**9**
formula	$C_{42}H_{32}Cu_2I_2N_2P_2$	$C_{38}H_{36}Cu_3I_3N_2P_2$	$C_{31}H_{27}CuINP_2$	$C_{23}H_{43}Cu_2I_2NP_2$	$C_{23}H_{43}Cu_3I_3NP_2$
Mw	1007.52	1153.95	665.92	776.40	966.84
Cryst. system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*C* 1 2/c 1	$P2_12_12_1$	$P2_1/n$	C2/c	C2/c
a (Å)	38.973(8)	10.185 (1)	15.983(3)	23.986(5)	15.373(1)
b (Å)	11.992(2)	13.224(3)	11.391(2)	13.948(3)	16.444(1)
c (Å)	17.704(4)	28.904(6)	16.357(3)	21.765(4)	14.240(1)
α (deg.)	90.00	90.00	90.00	90.00	90.00
β (deg.)	105.94 (1)	90.00	108.82(3)	109.18(3)	122.25(1)
γ (deg.)	90.00	90.00	90.00	90.00	90.00
Volume, Å^3	7956(3)	3893.2(12)	2818.7(10)	6877(2)	3044.3(4)
Z	8	4	4	8	4
T (K)	153(2)	148(2)	183(2)	133(2)	120(2)
D_{calcld}, g/cm^3	1.682	1.969	1.569	1.500	2.109
F(000)	3936	2216	1328	3056	1856
θ range, deg.	1.78-27.52	1.69-27.38	2.16-27.51	1.71-27.53	2.00-27.50
Index ranges	-50≤h≤50	-12≤h≤12	-20≤h≤17	-28≤h≤30	-19≤h≤17
	-15≤k≤15	-16≤k≤15	-14≤k≤14	-9≤k≤17	-15≤k≤21
	-18≤l≤22	-36≤l≤21	-14≤l≤20	-25≤l≤27	-16≤l≤18
GOF on F^2	1.358	1.238	1.377	1.692	1.248
R [I > 2ó(I)]	0.0498	0.0537	0.0424	0.0399	0.0464
R (all data)	0.0382	0.0431	0.0543	0.0501	0.0339

Computational Methods

All of the molecular orbital calculations were performed with the Titan (version 1.0.7) program at the B3LYP level using a LACVP** basis set. The geometry for single-point density functional theory (DFT) calculations was taken from the crystal structure of each complex.

Synthesis

L_1: 8-(diphenylphosphino)quinoline was synthesized similar to the reported procedure and NMR data of which are in agreement with the literature value.[35] To a solution of 8-chloroquinoline (1.63 g, 10 mmol) and 18-crown-6 (3.43 g, 13 mmol) in THF was added slowly a 0.5 M solution of potassium diphenylphosphine (24 mL, 12 mmol) in THF at -78°C. The mixture was allowed to stir at room temperature for 12 hrs and then poured into ice water carefully. A yellow precipitate was obtained by filtration and chromatographed on silica gel column with CH_2Cl_2 as eluent followed by recrystallization in CH_2Cl_2/CH_3CN to get 1.35 g white powder, yield 43%.

L_2: 2-[2-(diphenylphosphino)ethyl]pyridine was synthesized according to the reported procedure and the NMR data are in agreement with the literature value.[36]

L_3 and **L_4**: 2,6-bis((diphenylphosphino)methyl)pyridine and 2,6-bis((di-tert-butylphosphino)methyl)pyridine were synthesized according to the procedure described below, and used without purification by considering their stability in air.[37]

$Cu_2I_2(L_1)_2$ (**5**): To a CH_3CN/CH_2Cl_2 (20/10 mL) solution of **L_1** (313 mg, 1.0 mmol) was added CuI (190 mg, 1.0 mmol) in CH_3CN (15 mL). Red crystals were obtained after 3 days in 93% yield (470 mg). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.38 (d, *J* = 4.4 Hz, 1 H), 8.25 (d, *J* = 9.2 Hz, 1 H), 7.92 (t, *J* = 8.4 Hz, 1 H), 7.80 (t, J_1 = 7.2 Hz, J_2 = 6.4 Hz 1 H), 3.34 (d, *J* = 9.2 Hz, 4 H), 1.35 (d, *J* = 13.6 Hz, 36 H). ^{31}P-NMR (400 MHZ, $CDCl_3$): δ -29.8. Anal. calcd. for $C_{42}H_{32}Cu_2I_2N_2P_2$: C, 50.07; H, 3.20; N, 2.78. Found: C, 49.86; H, 3.17; N, 2.80.

$Cu_3I_3(L_2)_2$ (**6**): To a CH_3CN (20 mL) solution of **L_2** (325 mg, 1.1 mmol) was added CuI (210 mg, 1.1 mmol) in CH_3CN (20 mL) quickly without stirring, white crystals were obtained after 1 hour in 35% yield (150 mg). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.26 (s, 1H), 7.68 (t, *J* = 8.6 Hz, 1H), 7.42 (s, 4H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.23 (m, 6H), 3.45 (s, 2H), 2.89 (s, 2H). ^{31}P-NMR (400 MHz, $CDCl_3$): δ -16.2. Anal. calcd. for $C_{38}H_{36}Cu_3I_3N_2P_2$: C, 39.55; H, 3.14; N, 2.43. Found: C, 39.57; H, 3.10; N, 2.50.

CuI(L_3) (**7**): To a stirred solution of potassium diphenylphosphine (6.7 mL, 3.4 mmol) was added slowly a solution of 2,6-bis(chloromethyl)pyridine (0.30g, 1.7 mmol) in THF at -78°C. The mixture was stirred at room temperature for 2 hours and transferred into a drop funnel under nitrogen atmosphere. The slurry was dropped into a CH_3CN solution of CuI (324 mg, 1.7 mmol) and the mixture stirred for 2 hours. The complex **7** was then obtained as light yellow crystal by flash column chromatography using CH_2Cl_2:CH_3COOEt (v/v, 10:1) as eluent, followed by recrystallization from CH_2Cl_2/CH_3CN. Yield 41% (450 mg) for the two steps. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.57 (t, *J* = 7.6 Hz, 1H), 7.48 (m, 8H), 7.32 (t, *J* = 7.2 Hz, 4H), 7.21 (t, *J* = 7.2 Hz, 8H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 4H). ^{31}P-NMR (400 MHz, $CDCl_3$): δ -3.3. Anal. calcd. for $C_{31}H_{27}CuINP_2$: C, 55.91; H, 4.09; N, 2.10. Found: C, 55.34; H, 4.07; N, 2.15.

$Cu_2I_2(L_4)$ (**8**): To a stirred solution of 2,6-dimethylpyridine (300 mg, 2.8 mmol) in THF at -78°C was added slowly n-BuLi (1.6 M, 3.5 mL). The mixture was stirred at 45°C for 1 hour and followed by dropping di-tert-butylchlorophosphine (1.0 g, 5.6 mmol) at -78°C. The resulting solution was stirred overnight and then dropped into a solution of CuI (535 mg, 2.8 mmol) in CH_3CN. The mixture was stirred for two days, precipitate was filtered and the complex **8** was obtained as grey yellow crystal by recrystallization in CH_2Cl_2/CH_3CN. Yield 64% for the two steps. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 3.34 (d, *J* = 9.2 Hz, 4H), 1.35 (d, *J* = 13.6 Hz, 36H). ^{31}P-NMR (400 MHz, $CDCl_3$): δ 60.6, 34.0. Anal. calcd. for $C_{23}H_{43}Cu_2I_2NP_2$: C, 35.58; H, 5.58; N, 1.80. Found: C, 36.03; H, 5.64; N, 1.88.

$Cu_3I_3(L_4)$ (**9**): The complex **9** was obtained as green yellow crystals by gradient temperature sublimation of the complex **8** at high vacuum (10^{-6} Torr), yield: ~ 1%. Anal. calcd. for $C_{23}H_{43}Cu_3I_3NP_2$: C, 28.57; H, 4.48; N, 1.45. Found: C, 28.58; H, 4.35; N, 1.46.

Results and discussion

Synthesis and structures

Since the d^{10} electronic configuration of Cu(I) enforces no stereochemical demand, the coordination sphere is therefore largely determined by electronic and molecular mechanical factors. For example, mononuclear CuI(3-Mepy)$_3$ to polymer $[CuI(py)]_\infty$ (3-Mepy = 3-methylpyridine, py = pyridine) have been prepared from the simple combination of CuI and pyridine-type ligands in different molar ratios.[14,25] In our case, the complexes **5** and **6** were obtained at certain ratios of CuI to ligand, while the complexes **7** and **8** were obtained with unclear ratios. Although we have found that complex **7** was obtained no matter how the input CuI:**L_2** ratio is 2:1 or 1:1, it should be noted that the complex structure with a certain ligand may vary if forced by mass action law.[14]

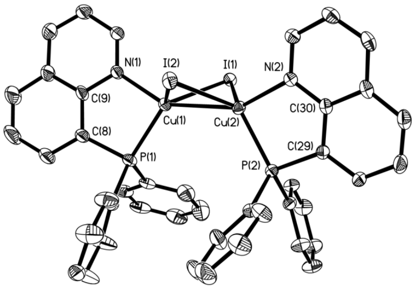


Fig. 1 ORTEP drawing of the complex **5** with ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Fig. 1 shows the perspective view of the dimeric complex **5**. Two Cu^I ions are bridged by two μ^2-I ions, and coordinated by two bidentate P^N ligands **L_1** additionally, each Cu^I ion is in a distorted tetrahedral geometry. The Cu(1)-Cu(2) distance is 2.631(37) Å, which is much shorter than those found in dimeric complexes with isolated P and N ligands (2.872-3.303 Å),[26] while comparable with those in complexes bridged by 1,8-nap (2.51-2.63 Å).[28,38] With such a short Cu-Cu distance, the dihedral angle between the Cu(1)-I(1)-Cu(2) and Cu(1)-I(2)-Cu(2) faces is 137.7°, thus the $\{Cu_2(\mu^2\text{-}I)_2\}$ core observed here is one of the most distorted cores.[39]

The reaction of CuI with **L_2** gives a trinuclear complex **6**. A perspective view of the structure is depicted in Fig. 2. The three Cu^I ions are in a trigonal planar array with two μ^3-I ions [I(1) and I(2)] above and below the plane, respectively, and one μ^2-I [I(3)) ion as bridge of one side of the triangle, while each of the other two sides is connected by a $\mathbf{L_2}$ ligand. The μ^3-I binds to the Cu with bond lengths of 2.7205 to 2.7996 Å, which is longer than those of μ^2-I does (2.6980 to 2.7095 Å). Furthermore, the Cu^{I} ions those bridged by μ^2-I ions have significantly shorter Cu-Cu separation of 2.5236 Å, suggests a metal-metal bonding character.

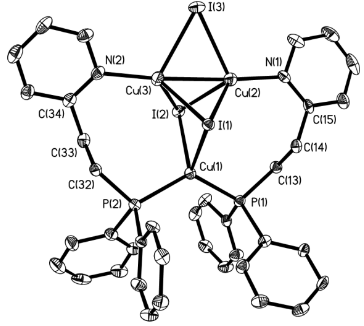


Fig. 2 ORTEP drawing of the complex **6** with ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

The complex **7** was found to be a mononuclear Cu(I) compound and has similar structure to its bromide one.[31] As shown in Fig. 3, the Cu^{I} ion adopts four coordinate, three of which are from the ligand $\mathbf{L_3}$. However, considering of the angle sums Σ{[P(2)-Cu(1)-P(1)]+[(P(1)-Cu(1)-I(1)]+[I(1)-Cu(1)-P(2)]} is 359.95°, the four atoms [P(1), P(2), I(1), and Cu(1)] are in the same plane. Herein the Cu^{I} ion has a much different coordination environment to quasi-tetrahedron for mostly reported Cu(I) complexes. The coordination of the Cu^{I} ion and the pyridine N atom is evident from the Cu-N length of 2.185(2) Å, which results in a dihedral angle of 121.0° between the pyridine ring and the plane that Cu seated.

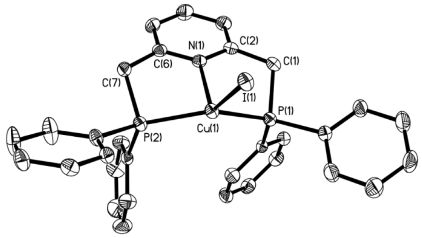


Fig. 3 ORTEP drawing of the complex **7** with ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

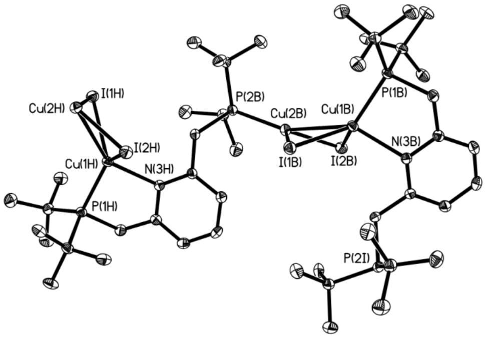


Fig. 4 ORTEP drawing of the repeating units of the complex **8** with ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

The complex **8** (Fig. 4) has a {$Cu_2(\mu^2\text{-}I)_2$} unit similar to that observed in the complex **5**, where the two Cu^{I} ions are bridged by two μ^2-I ions with Cu-Cu distance of 2.7913(8) Å and dihedral angle between the Cu(1B)-I(1B)-Cu(2B) and Cu(1B)-I(2B)-Cu(2B) faces of 142.3°. However, two kinds of Cu^{I} ion geometries found here; one Cu^{I} ion (Cu1B) adopts a distorted tetrahedral mode with two μ^2-I ions and one bidentate P^N fragment, while the other Cu^{I} ion (Cu2B) adopts a Y-shaped trigonal configuration with the two μ^2-I ions and one P atom. In the complex, the ligand $\mathbf{L_4}$ provide one bidentate P^N coordinate for one {$Cu_2(\mu^2\text{-}I)_2$} unit and the rest of P for another {$Cu_2(\mu^2\text{-}I)_2$} unit to form an extended one dimensional chain along the *b*-axis.

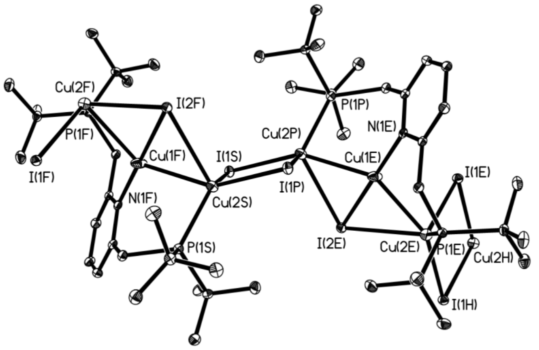


Fig. 5 ORTEP drawing of the repeating units of complex **9** with ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

The complex **9** is found to has an unprecedented polymeric chain that involves alternating {$Cu_2(\mu^2\text{-}I)_2$} and CuI unit coordinated by P atoms and pyridine N atom along the *ac*-axis, respectively. The {$Cu_2(\mu^2\text{-}I)_2$} unit has a parallelogram configuration with long Cu-Cu distance of 3.435(2) Å, which is different to those observed in complexes **5** and **8**, while similar to those reported ones with isolated P- and N- ligands. The {$Cu_2(\mu^2\text{-}I)_2$} and CuI units are connected by short Cu-Cu interaction of 2.570(2) Å and weak Cu-I interaction of 2.916(1) Å with μ^2-I bridges.

Photophysical properties

At room temperature, the solid samples of **5**, **6**, **7**, **8**, and **9** display photoluminescence with maximum wavelength at 664, 468, 564, 534, and 480 nm, PLQY of 1.6, 22.2, 16.2, 15.4, and 29.9 %, respectively (Fig. 6 and Table 2). The emissions have lifetimes on the microsecond scale, implying that these emissions are arising from triplet excited states. To gain insight into the emission properties, we performed single-point DFT calculations on the ground states of these complexes since such investigations have been proven to be very helpful in understanding the photophysical properties, which will be instructive to examine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the complex. Considering that calculations on polymeric complexes are costly we only examined HOMOs and LUMOs of the complexes **5**, **6**, and **7**. As shown in Fig. 8, the calculated energy levels around the frontier orbitals are similar to those reported CuI complexes, where the HOMOs are mainly focused on iodide and copper, while the LUMOs are on the N-heteroaromatic rings. With reference to the calculation results and previous work on the CuI complexes, these emissions could be ascribed to transitions from mixed XLCT and MLCT excited states.

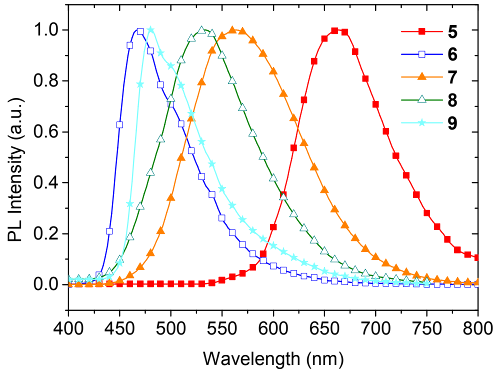


Fig. 6 Emission spectra of the complexes **5-9** in solid state (λ_{ex} = 380 nm).

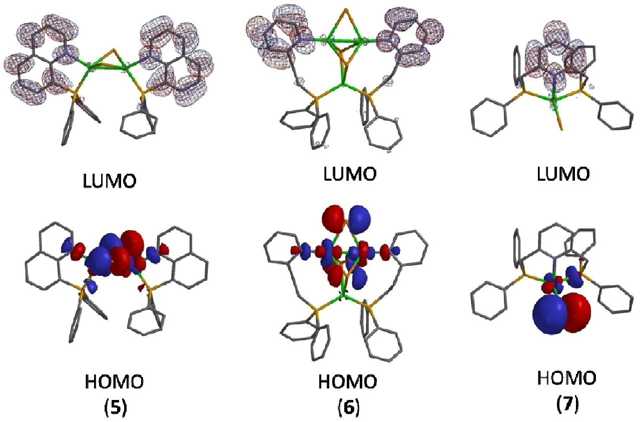


Fig. 7 Molecular orbitals of the complexes **5-7** calculated by Titan (version 1.0.7) using geometry that obtained from single crystal X-ray diffraction.

Table 2 Photophysical properties of the complexes **5-9**

	Solid Sample					Solution Sample				
	PLQY (%)	λ_{max} (nm)		Lifetime (μs)		PLQY (%)	λ_{max} (nm)		Lifetime (μs)	
		RT	77K	RT	77K		RT	77K	RT	77K
5	1.6	664	678	0.5	51.6/23.8	-	-	652	-	100.7/23.1
6	22.2	468	462	16.1/4.1/0.9	53.2/27.4	19.5	505/650	442	0.8	47.4/34.4
7	16.2	564	598	8.4/3.5	103.2	1.3	363/537	548	0.4	208.3/66.9
8	15.4	534	534	6.8/3.2/1.2	211.5/78.3	1.3	363/609	504	0.5	189.6/65.8
9	29.9	480	484	2.8/0.4	91.0/36.9	-	-	-	-	-

As the temperature decreased to 77 K, all the complexes have similar emission spectrum to that observed at room temperature and less than 20 nm blue-shifted maximum excitation wavelengths, except for the complex **7**. The complex **7** has maximum excitation and emission wavelengths around 404 and 598 nm at 77 K, which is 46 nm blue-shifted and 34 nm red-shifted compared to its excitation and emission at room temperature, respectively. With such a temperature-dependent photoluminescent property, the change in sample colour and emission colour can be recognized by naked eyes. Based on literatures,[40,41] luminescence of copper(I) complex is very sensitive to rigidity, due to a divalent copper characteristics in excited state that leading to structural reorganization from tetrahedral to a square-planar geometry.

The complex **9** is not stable in solution, as CuI precipitates when it dissolved, thus we measured only the complexes **5-8** in solution. The four complexes display intense emissions with long lifetimes in 2-MeTHF glassy solution at 77 K. Comparing to the spectra of solid sample at 77 K, all complexes have blue-shifted maximum emission wavelength, i.e., 26, 20, 50, and 30 nm for the complexes **5**, **6**, **7**, and **8**, respectively. At room temperature, no visible emission was found for the complexes **5-8** in 2-MeTHF.

Due to a divalent copper characteristics having square-planar geometry in excited state, copper(I) complex usually shows weak emission in solution at room temperature, as the excited Cu(II) center is exposed to and could be attacked by solvent molecules, leading to non-radiative transition. In our case, no visable emission was observed for the complex **5** in CH_2Cl_2 solution. Excitation of **7** or **8** at 300 nm gave weak green or red emission with peak around 537 or 609 nm, as well as an additional emission peak around 363 nm, respectively. It's interesting to note that the complex **8** has a low energy emission that usually observed in CuI complex with short Cu-Cu interaction. However, the Cu-Cu distance observed here is 2.7913(8) Å. With the Cu-Cu distance and emission peak at 363 nm that may come from ligand in mind, it is attempting to assign the weak red emission as decomposed species. The photophysical property of the complex **6** in CH_2Cl_2 solution also deserves attention. In addition to the emission around 500 nm that similar to the one observed in solid state at room temperature, an emission shoulder around 650 nm was examined, which has a similar excitation spectrum to the emission at 500 nm (Fig. 8). Since the shortest Cu-Cu distance in the complex **6** was examined as 2.5236(11) Å, it may reasonable to assign this emission to ^{3}CC excited state.

It should be noted that we have checked the possibility whether these compounds could be used in chemical vapour deposition (CVD) based OLEDs, for example, the quantum yield of the compound **5** is too low (1.6% in solid), the compounds **6** and **7** decomposed during the thermal gradient sublimation, the compound **8** converted to the emissive compound **9** while with extremely low yield (~1%). Unfortunately, these compounds may not good candidate for

CVD based OLEDs. Searching for new CuI based compound for OLEDs are in progress.

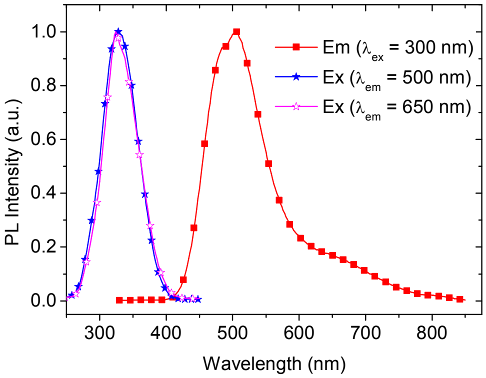


Fig. 8 Excitation (for emissions at 500 and 650 nm) and emission (excitation wavelength of 300 nm) spectra of the complex **6** in dichloromethane solution at room temperature

Conclusions

Two P^N type ligands $\mathbf{L_1}$ and $\mathbf{L_2}$, and two P^N^P type ligands $\mathbf{L_3}$ and $\mathbf{L_4}$ were synthesized and their CuI based complexes **5-9** have been prepared. X-ray crystallographic studies indicate that rich structures such as mononuclear, binuclear, trinuclear and polynuclear complexes have been obtained. All the complexes are emissive with emission colour varied from blue to red and PLQY from 1.6 to 29.9 % in solid state. Room temperature and low temperature (77 K) emissions and lifetimes, as well as single-point DFT calculations have been examined on these CuI complexes, indicating that the transitions are mainly originated from triplet XLCT, MLCT, and/or CC excited states.

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Notes and references

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†Electronic Supplementary Information (ESI) available: X-ray crystallographic files in CIF format are all available. CIFs have also been deposited at the Cambridge Crystallographic Database Centre and may be obtained from http://www.ccdc.cam.ac.uk by citing reference codes 981184-981188 for compounds **5-9**, respectively.

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A series of CuI complexes with P^N or P^N^P ligand showing rich structural and photophysical properties were synthesized and studied.