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Synthesis, crystal structures and photophysical properties of novel copper(I) complexes with 4-diphenylphosphino-1,5-naphthyridine ligands

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A R T I C L E I N F O

ABSTRACT

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Keywords: Copper(1) complexes 1,5-Naphthyridine HOMO-LUMO energy gaps Red-shifts Florescence Two new copper(I) complexes $[Cu(L^1)_2]PF_6$ (L^1 =4-diphenylphosphino-1,5-naphthyridine, **1**) and $[Cu(L^2)_2]$ PF₆ (L^2 =4-diphenylphosphino-8-methyl-1,5-naphthyridine, **2**), have been prepared and characterized. In each of them, the coordinate geometry of Cu atom is a distorted square planar configuration with bond distances and angles in the normal range. Moreover, compound **2** features one-dimensional zigzag chains which are cross-linked by the metal complex cations and PF₆⁻ anions through hydrogen bonding interactions. The HOMO-LUMO energy gaps of **1**-**2** estimated by the cyclic voltammetry (CV) show values in the order of **1**>**2**. Both **1** and **2** show low-energy bands ranging from 360 to 430 nm and available florescence in the solid state at room temperature with λ_{max} = 532–541 nm. The UV-vis absorption spectra of **1**-**2** show obvious red-shifts compared with those of the corresponding quinoline containing Cu(I) complexes [Cu(QN)₂]PF₆.

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Copper(I) complexes have garnered much attention because of their economical and environmental utilization in organic light emitting diodes (OLEDs) [1]. Tremendous efforts have been devoted to tune its fluorescence color to the red or blue region [2]. Among them, the Cu(I) complex based on the asymmetrical P^N ligand processes a considerably higher reduced state and exited state stability than the analogous complexes based on symmetrical diimine or diphosphine ligand [3]. In recent years, 8-(diphenylphosphino)-quinoline (ON) ligands were extensively used for crystallization of Cu(I). Ni(I). Ru(II) and Pd(II) compounds [3,4], whereas naphthalenephosphine based coordination compounds were seldom reported. 4-Diphenylphosphino-1,5-naphthyridine, which can be regarded as a combination of the bidentate 1,5-naphthyridine and 4-(diphenylphosphino) pyridine, exhibit various coordination modes, high symmetry and large conjugated π -system that may lead to special physical properties and potential applications. Additionally, the difference of redox properties between naphthyridine and quinoline provides a significant impetus for our continued exploratory synthesis [5]. Here, we report the synthesis, crystal structures and photophysical properties of two novel Cu(I) complexes $[Cu(L^1)_2]PF_6$ ($L^1 = 4$ -diphenylphosphino-1,5-naphthyridine, 1) and $[Cu(L^2)_2]PF_6$ ($L^2 = 4$ -diphenylphosphino-8-methyl-1,5naphthyridine, **2**). To the best of our knowledge, there are no reports of such work based on 1,5-naphthalenephosphine ligands.

The new ligands, L^1 and L^2 were synthesized by the reactions of Ph₂PLi [6] with the chloro-substituted starting compounds (**Clnd** and **Clmnd**) [7], which were different from the reported method [8]. The homoleptic complexes $[Cu(L^1)_2]PF_6$ and $[Cu(L^2)_2]PF_6$ were obtained by the reaction of L^1 and L^2 with $[Cu(CH_3CN)_4]PF_6$ in CH₃OH/CHCl₃ [9] (Scheme 1), respectively.

The ¹H NMR spectrum of **1** and **2** shows a symmetric signal set, and only one single assigned to the proton of the methyl group in the 4-position on a naphthyridine ring at δ 2.9 appeared. The ³¹P NMR spectrums of **1** and **2** show a relatively broad signal at δ – 18.0 and δ – 17.2 result from quadrapolar relaxation arising from the copper nucleus [10], whereas the signal of free ligands is sharp at δ – 15.4 and δ – 15.1, respectively. The elemental analysis (C, H, and N) and mass spectrometric data are in excellent agreement with the compositions of the ligands [9].

The X-ray diffraction measurements of single crystal of **1** were carried out at room temperature (RT) [11] and low temperature (LT) [12], respectively. Complex **1(RT)** crystallizes in the monoclinic system P_{21}/c space group with two molecules per asymmetric unit (Fig. 1a) and the presence of two hexafluorophosphate anions (PF₆⁻) providing charge balance. The copper(I) exhibits highly distorted tetrahedral geometry arising from the intraligand chelate angles N1–Cu1–P1 in **I** and N7–Cu2–P4 in **II** being 88.47 (18) (deg) and 87.92 (17) (deg), respectively. However, the P1–Cu1–P2 angle 118.61 (8) (deg) in **I** and the P4–Cu2–P3 angle 122.04 (8) (deg) in **II**, have opened up due to the steric effects from the bulky ND ligands. The average Cu–N (2.055 Å) and Cu–P (2.225 Å) bond distances are comparable to those reported for $[Cu(QN)_2]PF_6$ (QN = 8-diphenylphosphino quinoline)

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Scheme 1. Synthesis of ligands and corresponding Cu(I) complexes.



Fig. 1. Views of 1(RT), hydrogen atoms and PF₆⁻ anions are omitted for clarity. (a) Coordination environment of Cu atom; (b) crystal packing structure with polyhedron along the *a*-axis, green dash lines indicated hydrogen bonds.

(2.072 and 2.225 Å) [4f]. The selected bond lengths and bond angles are given in Table 1. One of the two PF_6^- anions is position-disordered even though in the low temperature (Fig. S1).

In the crystal packing, the metal complex cations and PF_6^- anions are connected by weak C–H–F–P hydrogen bonds, mainly distributed along the *a*-axis (Fig. 1b). Ten H–-F distances are shorter than 2.6 Å with the shortest one of 2.28 Å (Table S1), confirming their significant role played in crystal cohesion [13]. Detailed analysis of the structural data reveals the presence of three sets of π – π stacking of naphthyridine ligands between neighboring cations, for which the centroid–centroid contact is calculated to be 3.75 Å (yellow dash line). The second naphthyrine ligand is parallel to the naphthyrine chelate of the adjacent molecule where an even stronger pairwise π – π stacking is observed with the centroid–centroid contact being reduced to 3.72 Å (blue dash line). The third one is the π – π stacking between the phenyl groups of the two Ph₂P segments on each of the two molecules in one asymmetric unit. Their reduced centroid–centroid contacts of 3.78–3.95 Å symbolized the formation of a non-negligible intra-molecular π – π stacking interaction (brown dash line), which are analogous to those reported in the Ru(II) and Cu(I) complexes containing phosphine ligands [3d, 3e]. It is noted that PF₆⁻ anions form a zigzag chain along the *a*-axis as the Cu atoms (Fig. S2).

Structural analysis of **2** at RT [14] reveals that it crystallizes in *C*2/*c* space group, which is different from complex **1(RT)**, as shown in Table S2. In the structure of compound **2**, half of the molecule is generated by inversion (Fig. 2a). Just as in the case of **1**, the Cu⁺ ions are coordinated by two bidentate L^2 ligands and have a four-coordinate structure with a highly distorted tetrahedral geometry. The Cu–N and Cu–P bond lengths are 2.071 (3) Å and 2.2443 (11) Å, respectively, which are similar to those of **1**. The metal complex cations and PF₆⁻ anions are connected by weak C-H––F-P hydrogen bonds and form

Table 1			
Selected bond lengths	(Å) and angle	(deg) for 1(RT)	and 2 .

	1(RT)	2	
Cu1-N1/Cu2-N7	2.057 (6)/2.046 (5)	Cu-N2	2.071 (3)
Cu1-N4/Cu2-N6	2.062 (5)/2.049 (6)	Cu-N2*	2.071 (3)
Cu1-P1/Cu2-P4	2.222 (2)/2.218 (2)	Cu–P1	2.2443 (11)
Cu1-P2/Cu2-P3	2.232 (2)/2.227 (2)	Cu-P1*	2.2443 (11)
N1-Cu1-N4/N7-Cu2-N6	107.9 (2)/107.5 (2)	N2-Cu-N2*	110.08 (17)
N1-Cu1-P1/N7-Cu2-P4	88.47 (18)/87.92 (17)	N2-Cu-P1	87.35 (9)
N1-Cu1-P2/N7-Cu2-P3	124.25 (16)/128.46 (16)	N2-Cu-P1*	124.91 (10)
N4-Cu1-P1/N6-Cu2-P4	133.89 (16)/126.67 (17)	N2*-Cu-P1	124.91 (10)
N4-Cu1-P2/N6-Cu2-P3	87.78 (16)/87.86 (19)	N2*-Cu-P1*	87.35 (9)
P1-Cu1-P2/P4-Cu2-P3	118.61 (8)/122.04 (8)	P1-Cu-P1*	125.36 (6)
Cu1-N1-C19-C20/Cu2-N7-C80-C79	-5.7 (8)/-6.0 (7)	Cu-N2-C8-C1	2.5 (5)
Cu1-P1-C19-C20/Cu2-P4-C79-C80	6.3 (5)/10.9 (5)	Cu-P1-C1-C8	-6.5 (3)
Cu1-N4-C40-C33/Cu2-N6-C60-C53	-2.8 (8)/-3.6 (9)	Cu-N2*-C8-C1	2.5 (5)
Cu1-P2-C33-C40/Cu2-P3-C53-C60	8.7 (5)/9.7 (6)	Cu-P1*-C1-C8	-6.5 (3)



Fig. 2. Views of **2**, hydrogen atoms, solvent (C_5H_5O) molecules and PF_6^- anions are omitted for clarity. (a) Coordination environment of Cu atom; (b) crystal packing structure with polyhedron through the bonding interactions along the *a*-axis, green dash lines indicated hydrogen bonds.

one-dimensional zigzag chains along the *c*-axis (Fig. 2b). Furthermore, the zigzag chains are packed together through face-to-face π - π stacking between naphthyrine rings from adjacent chains along the *a*-axis and the interplanar distance between the naphthyrine rings is 3.89 Å (blue dash line).

Electrochemical behaviors of the two complexes had been studied in acetonitrile solutions, along with the comparative complexes [Cu(QN)₂]PF₆ [4f]. Similar to guinoline-based Cu(I) complex, both 1 and 2 display irreversible and multiple oxidation peaks that might be attributed to multiple electron-transfer originating from the Cu(I) center and the P-coordinating groups (Fig. S3a). As Table 2 shows, the first oxidation potentials for the Cu^{II/I} redox couple became more positive in the order of $[Cu(QN)_2]PF_6$ (+0.43 V)<2(+0.54 V)< 1(+0.59 V). These indicate that the naphthyridyl backbone stabilize the Cu(I) oxidation state more than quinolyl backbone, owing to a better π -acceptability of the naphthyridines. During the cathodic scan, all of the three complexes show irreversible ligand-based reduction processes with peak potentials at -2.28, -2.00, -1.94 V and the onset potentials for reduction are -2.18, -1.87, -1.88 V, respectively. HOMO and LUMO levels were estimated from the onset potentials by comparison to ferrocene (4.8 eV versus vacuum) [15]. Electron affinities (LUMO) were estimated from the onset of the reduction wave $(E_{LUMO} = -(4.8 + E_{ref} + E_{onset(red)}))$ and ionization potential (HOMO) was estimated from the onset of the oxidation wave $(E_{HOMO} = -(4.8 + E_{ref} + E_{onset(ox)}))$. The data of E_{HOMO} , E_{LUMO} , and gaps between the LUMO and HOMO energy levels are presented in Table 2. Both the energy gaps of 1 and 2 are narrower than that of [Cu(ON)₂]PF₆, this may ascribe to the introduction of electronwithdrawing nitrogen atoms to the phenyl rings of the naphthyridyl ligands.

The UV/vis absorption spectra of complexes **1** and **2** in CH_2Cl_2 and the emission (λ_{exc} = 370 nm) in solid crystal at 298 K are shown in Fig. 3. To further elucidate the origin of these peaks, absorption and fluorescent spectrums of the free ligand are also measured, as shown in Table S3. Complexes **1** and **2** show very similar absorption spectra with the short wavelength region below 320 nm, being due to ligandcentered (LC) transitions of the iminephosphine ligands. In contrast, the low-energy bands ranging from 360 to 430 nm cannot be found in the absorption spectrum of the free ligand, which indicates that the corresponding states exhibit metal-to-ligand charge transfer (MLCT) character. The absorption spectra of 1 and 2 overall redshift apparently compared with that of [Cu(QN)₂]PF₆, indicating the narrower HOMO-LUMO electronic energy gaps in 1 and 2, which are consistent with the results estimated from the CV measurements. Furthermore, the HOMO-LUMO electronic energy gaps of **1**, **2** and $[Cu(QN)_2]PF_6$ calculated by the absorption onsets obtained from the UV-vis absorption spectra are 2.52, 2.39 and 2.65 eV, respectively, which are comparable with those estimated from the CV measurements. Complexes 1 and 2 are not emissive in solution, but their solid state fluorescent emissions are available. The emission peaks of **1** ($\lambda_{max} = 541 \text{ nm}$) and **2** ($\lambda_{max} = 532 \text{ nm}$) blueshift apparently compared with that of $[Cu(QN)_2]PF_6$ ($\lambda_{max} = 640 \text{ nm}$) [4f]. This may be because the emission of copper(I) complexes with asymmetrical P^N ligand is mainly dependent on the nature of the P^N ligand. Meanwhile, the emission peak of 2 shows 9 nm blue-shift compared to that of 1. The reason for this can be explained as that the sterically active substituent prevents the excited state conformation change from a tetrahedral to a more flattened structure, which has a lower MLCT energy [2b].

In summary, two new cuprous complexes containing phosphinonaphthyrine ligands were successfully prepared and characterized. The X-ray determinations reveal that the coordinate geometry of the Cu atoms are distorted square planar configuration. These Cu(I) complexes show different crystal packing configuration arising from the steric effect of the methyl substituent on naphthyridine moiety. Not only electrochemistry properties, but also photophysical properties show that the HOMO–LUMO energy gaps of **1–2** are narrower than that of $[Cu(QN)_2]PF_6$. The peak emission of complex **1–2** are shifting to the blue region compared to that of $[Cu(QN)_2]PF_6$. These results will expand the design artifices of florescent complexes which can emit lights covering a full range of visible colors.

Acknowledgments

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Electrochemical data^a for **1**, **2** and $Cu(QN)_2^+$.

Compd.	$E_{ref}(V)$	Oxidation(V)		Eonset(ox)	E _{HOMO} Reduction	Reduction	iction(V) E _{onset(r}		onset(red) E _{LUMO}	$E_g^{el} \; (eV)^b$	$E_g^{opt}(eV)^c$
		E ₂	E1	(V)	(eV)	E1	E ₂	(V)	(eV)		
1	0.076	0.89	0.59	0.44	-5.32	- 1.94	-2.12	-1.88	- 3.00	2.32	2.52
2	0.078	0.85	0.54	0.40	-5.29	-2.00	-2.20	-1.87	-3.00	2.27	2.39
$Cu(QN)_2^+$	0.082	0.77	0.43	0.31	-5.19	-2.28	-2.47	-2.18	-2.70	2.49	2.65

^a Redox potential recorded in acetonitrile solution with 0.1 M TBAP as supporting electrolyte; scan rate = 100 mV/s.

^b Band gaps obtained from electrochemical data.

^c Band gaps obtained from UV/Vis absorption spectrum.



Fig. 3. Absorption and photoluminescence spectra of 1 and 2 at room temperature. Absorption (left): CH₂Cl₂, 1 cm cell. Emission (right): $\lambda_{exc} = 370$ nm, solid.

Appendix A. Supplementary data

CCDC 833120 for 1 and 833123 for 2 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix A. Supplementary data

Supplementary materials related to this article can be found online at doi:10.1016/j.inoche.2011.12.028.

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 [7] Synthesis of L¹: A solution of PPh₂Li (960 g, 5 mmol) in THF (5 mL) was added dropwise to a solution of Clnd (820 mg, 5 mmol) in 20 ml THF at room temperature under argon atmosphere in half an hour. The mixture was stirred for 20 h at room temperature. The solvent was then removed and 10 mL of water was added. The resultant solution was extracted by diethyl ether (3X15 mL). The combined organic layer was concentrated and purified by column chromatography producing 500 mg (32% yield) of a yellow powered solid. Anal. Calc. for L^1 (C₂₀H₁₅N₂P₁, 314.1): C, 76.42; H, 4.81; N, 8.91. Found: C, 76.70; Calc. 101 L ($_{20115W2r1}$, 514.1). C, 76.42, n, 4.61, N, 6.91, Follin, (, 76.76), H, 5.08; N, 8.89%. ESI-MS: m/z = 315 [M]⁺, ¹H NMR (300 MHz, CDCl₃) (ppm): δ 8.87 (dd, J=4.1, 1.6 Hz, 1H), 8.81 (d, J=4.3 Hz, 1H), 8.40 (tt, J=8.5, 1.6 Hz, 1H), 7.60 (dd. J = 8.5, 4.2 Hz, 1H), 7.39–7.26 (m, 10H), 7.00 (dd. J = 4.3, 3.2 Hz, 1H). ³¹P-NMR (CDCl₃; d, ppm): $\delta - 15.4$ (s). Synthesis of **L**²: This compound was synthesized in the same manner as L^1 , except that **Climd** (979 mg, 5.5 mmol) was used instead of **Clnd**. The product (L^2) was obtained as a yellow powered solid. Yield: 40% (722 mg). Anal. Calc. for L^2 ($C_{21}H_{17}N_2P_1$, 328.1): C, 76.82; H, 5.22; N, 8.53. Found: C, 76.93; H, 4.68; N, 8.35%. ESI-MS: m/z = 329 [M]⁺. ¹H NMR (300 MHz, CDCl₃) (ppm): δ 8.81 (dd, J = 4.3, 0.8 Hz, 1H), 8.71 (d, J = 4.3 Hz, 1H), (7.43 (d, j = 4.3 Hz, 1H), 7.35–7.25 (m, 10H), 6.98 (dd, j = 4.3, 3.1 Hz, 1H), 2.83 (s, 3H). ³¹P-NMR (CDCl₃; d, ppm): $\delta - 15.1$ (s).
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- Synthesis of 1: L¹ (408 mg, 1.3 mmol) in 10 mL chloroform was added to a solution [9] of [Cu(CH₃CN)₄]PF₆ (241.8 mg, 0.65 mmol) in methanol (30 mL) under nitrogen atmosphere. The reaction mixture was stirred for 2 h at room temperature and then filtered. The filtrate was further reelingly evaporated to remove the solvent and the crude product was obtained as a red powder. Red crystals of 1, which were suitable for X-ray diffraction analysis, were obtained by recrystallization from tetrahydrofuran/methanol/ethylether (2:1:6 v/v/v) in a yield of 848 mg (78%). Anal. Calc. for 1 (C₄₀H₃₀CuF₆N₄P₃, 836.8): C, 57.39; H, 3.61; N, 6.69. Found: C, 57.18; H, 3.77; N, 6.53%. ESI-MS: $m/z = 691 [Cu(L^1)_2]^+$. ¹H NMR (500 MHz, DMSO-*d*₆) (ppm): δ 9.26 (d, *J* = 4.3 Hz, 1H), 8.78 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.63 (dd, J = 4.5, 1.3 Hz, 1H), 8.11 (d, J = 4.2 Hz, 1H), 7.87 (dd, J = 8.6, 4.6 Hz, 1H), 7.53–7.38 (m, 10H). ³¹P-NMR (CDCl₃) (ppm): δ – 18.0 (br). Synthesis of **2**: This compound was synthesized in the same manner as 2, except that L^2 (328 mg, 1 mmol) was used instead of L¹. Orange crystals of 2 containing one molecule of tetrahydrofuran, which were suitable for X-ray diffraction analysis, were obtained by recrystallization from tetrahydrofuran/methanol/ethylether (2:1:6 v/v/v) in a yield of 586 mg (62%). Anal. Calc. for 2.C5H5O (C46H38- $(ppm): \delta - 17.2 (br).$
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- X-ray diffraction datas were collected at 293 K on a Nonius CAD4 area detector [11] using grafite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Intensity data sets were corrected for absorption by a psi-scan procedure and the structures was determined by direct methods, with SHELXL-1997. Nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were placed at ideal positions and allowed to ride.
- [12] X-ray diffraction datas were collected at 223 K on a Rigaku Saturn area detector using grafite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Intensity data sets were corrected for absorption by a multi-scan procedure and the structures was determined by direct methods, with SHELXL-1997. Nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were placed at ideal positions and allowed to ride
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