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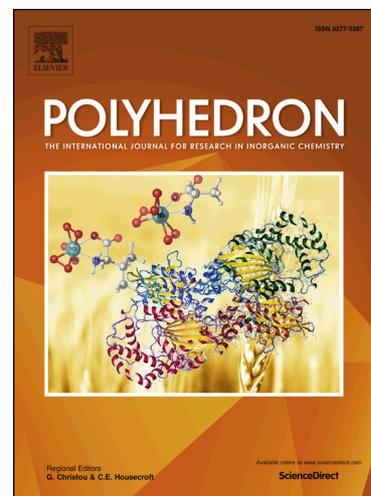
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Synthesis, Structures and Photophysical Properties of Cu(I)

Phosphine Complexes with Various Diimine Ligands

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Abstract: A series of triphenylphosphine Cu(I) complexes with various diimine ligands, [Cu(N-N)(PPh₃)₂](ClO₄) [N-N = **dmp** (**2**); **Ph₂Phen** (**3**); **Ph₂dmp** (**4**); **dpq** (**5**); **dppz** (**6**); **phenCN** (**7**); **phenOH** (**8**)] are synthesized by the ligand substitution reactions of [Cu(MeCN)₄](ClO₄) with 2 mole equiv. of PPh₃ ligand and 1.2 mole equiv. of diimine ligand. {Cu(**dpq**)[P(XPh)₃]₂}(ClO₄) [X = Me (**5a**); OMe (**5b**); Cl (**5c**)] and {Cu(**phenOH**)[P(XPh)₃]₂}(ClO₄) [X = Me (**8a**); OMe (**8b**)] are also obtained by using various substituted phosphine ligands. These mixed-ligand complexes have been characterized using ¹H and ³¹P NMR spectroscopy, IR spectroscopy, mass spectrometry and elemental analysis. Three of these complexes have been structurally characterized by X-ray crystallography. The photophysical and electrochemical properties of these complexes have been studied. These complexes exhibit MLCT phosphorescence with emission energy, lifetimes and quantum yields showing strong dependence on the nature of diimine and phosphine ligands. In particular, both the electronic and steric effects of the substituting groups in phosphine ligands are also found to affect the emission properties of the complexes. Our study provides structural-properties information for the future design of luminescent Cu(I) complexes.

Keywords: Luminescent properties; Cu(I) complexes; Crystal structures; Electrochemistry

Introduction

Phosphorescent complexes of noble metals, especially of iridium(III) and platinum(II) complexes, have been investigated extensively due to their extensive uses as emissive dopants in organic light-emitting diodes (OLEDs).^[1] These phosphorescent materials are superior to fluorescent materials because they can harvest both singlet and triplet excitons in electroluminescence processes, leading to the high internal quantum efficiency.^[2] These metals are, however, very expensive, since their earth abundance are rather limited.

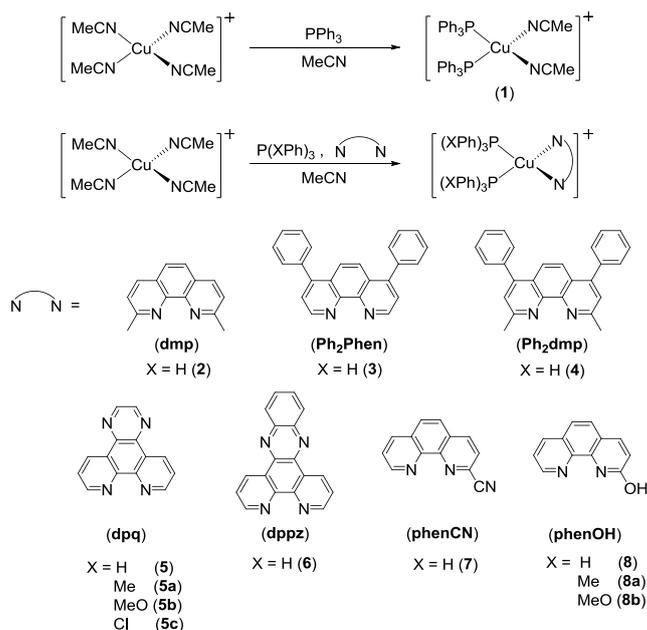
To develop easily accessible and sustainable luminescent materials for OLEDs, luminescent Cu(I) complexes have received increasing attention in recent years due to their high relative abundance, low cost, and environmentally friendly feature.^[3] To improve the luminescent properties of Cu(I) bis(diimine) $[\text{Cu}(\text{N-N})_2]^+$ complex system, mixed-ligand Cu(I) complexes with triphenylphosphine (PPh_3) and various diimine ligands have been developed; these complexes are demonstrated to be promising alternatives for OLEDs *due* to their excellent emissive properties.^[3] Until now, a number of mixed-ligand Cu(I) diimine phosphine complexes such as $[\text{Cu}(\text{N-N})(\text{P-P})]^+$ system (P-P = various bis(phosphine) ligands) have been reported and their emission properties have been investigated in various solvents and different temperatures.^[4] Some of these complexes, particularly those with bulky PPh_3 and diimine ligands, are found to be excellent emitters as their charge-transfer (CT) excited states are not quenched by solvent-induced exciplex.^[3,4] Also, the sterically demanding ligands can impede geometric relaxation from tetrahedral to square planar in the excited state.^[5] Though the spin-orbit coupling (SOC) effect of Cu(I) ion is weak, compared with that for iridium metal ($\zeta_{\text{Cu}} = 857 \text{ cm}^{-1}$ vs. $\zeta_{\text{Ir}} = 3909 \text{ cm}^{-1}$),^[6] the singlet state can be thermally activated at the expense of the triplet state due to the small energy gaps $\Delta E(\text{S}_1\text{-T}_1)$ between the lowest singlet state and lowest triplet state in some emissive Cu(I) complexes, leading to efficient thermally activated delayed fluorescence (TADF) at ambient temperature.^[7] With the capability to harvest both the singlet and triplet excitons, Cu(I) complexes with TADF behavior have been considered as promising emissive dopants in electroluminescent devices over the past few years.^[8]

To further enhance the excited-state and emission properties of Cu(I) complexes, much attention has been paid to design various diimine ligands with sterically hindered substituents in various heteroleptic Cu(I) systems to impede the Jahn-Teller distortion in the excited state.^[9] However, related works on altering the substituents of the PPh_3 are much less reported.^[10] Herein, we report the synthesis, structures of a series of Cu(I) complexes with various diimine and phosphine ligands. In addition, their photophysical and electrochemical properties have also been investigated in detail.

Results and discussion

Synthesis and Characterizations

The precursor complex $[\text{Cu}(\text{MeCN})_4](\text{ClO}_4)$ was prepared according to the literature procedure.^[11] Through the ligand substitution reaction of the precursor with 2 mole equiv. of PPh_3 ligand afforded initially the complex $[\text{Cu}(\text{MeCN})_2(\text{PPh}_3)_2]^+$ (**1**)^[12] and it then reacted with 1.2 mole equiv. of different diimine ligands in acetonitrile solution at ambient temperature to give the Cu(I) triphenylphosphine complexes with various diimine ligands, $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2](\text{ClO}_4)$ [N-N = **dmp** (**2**); **Ph₂Phen** (**3**); **Ph₂dmp** (**4**); **dpq** (**5**); **dppz** (**6**); **phenCN** (**7**); **phenOH** (**8**)] (Scheme 1). Using a similar synthetic strategy except that the substituted phosphine ligands are used instead of PPh_3 , $\{\text{Cu}(\text{dpq})[\text{P}(\text{XPh})_3]_2\}(\text{ClO}_4)$ [X = Me (**5a**); OMe (**5b**); Cl (**5c**)] and $\{\text{Cu}(\text{phenOH})[\text{P}(\text{XPh})_3]_2\}(\text{ClO}_4)$ [X = Me (**8a**); OMe (**8b**)] are obtained. After slow evaporation of the solutions of these complexes, analytically pure complexes were isolated as yellow or orange microcrystalline solids. All these mixed-ligand complexes have been characterized using ^1H and ^{31}P NMR spectroscopy, IR spectroscopy, mass spectrometry and elemental analysis. The structures of **2**, **5c**, and **7** have also been confirmed by X-ray crystallography.



Scheme 1. Synthetic route for $[\text{Cu}(\text{MeCN})_2(\text{PPh}_3)_2]^+$ (1) and $\{\text{Cu}(\text{N-N})[\text{P}(\text{XPh})_3]_2\}^+$ (2-8).

X-ray Crystal Structure Determination

By slow evaporation of solutions of the complexes, single crystals of **2**, **5c** and **7**, with quality suitable for X-ray crystal structure determination were obtained. Perspective drawings of the cations of these complexes are shown in Figure 1. The selected bond lengths (Å) and angles (°), and the structure determination data are summarized in Table 1 and Table S1, respectively. As shown in the structures of **2**, **5c** and **7**, all these complexes display distorted tetrahedral geometry (Figure 1). The bite angles of diimine ligands are in the range of 79.4(5)–80.5(2)°, which are smaller than 90°. This is due to the steric requirement of chelating ligands and is commonly observed in related diimine transition metal complexes.^[13] In addition, these Cu(I) complexes show P–Cu–P bond angles ranging from 123.57(7)–124.21(8)°, which are similar to those in the related bis(phosphine) Cu(I) complexes.^[14] Comparing the dihedral angles between P–Cu–P and N–Cu–N planes of these complexes [**2**): 96.7(1)°; (**5c**) 90.7°; (**7**) 81.7°], a smaller dihedral angle is observed in **7**, which is probably due to the steric effect of asymmetric **phenCN** ligand in **7**. The Cu–N and Cu–P bond distances are in the typical range of 2.068(6)–2.128(13) Å and 2.211(2)–2.284(4) Å respectively, which are comparable with those in the related Cu(I) complexes.^[14] Except for **7**, **2** and **5c** show similar Cu–N bond distances. The deviation of the Cu–N bond distance (Cu–N1: 2.104(5) Å, Cu–N2: 2.082(5) Å) in **7** is attributed to the asymmetrical chemical environment and electron-withdrawing cyano group of **phenCN** ligand.

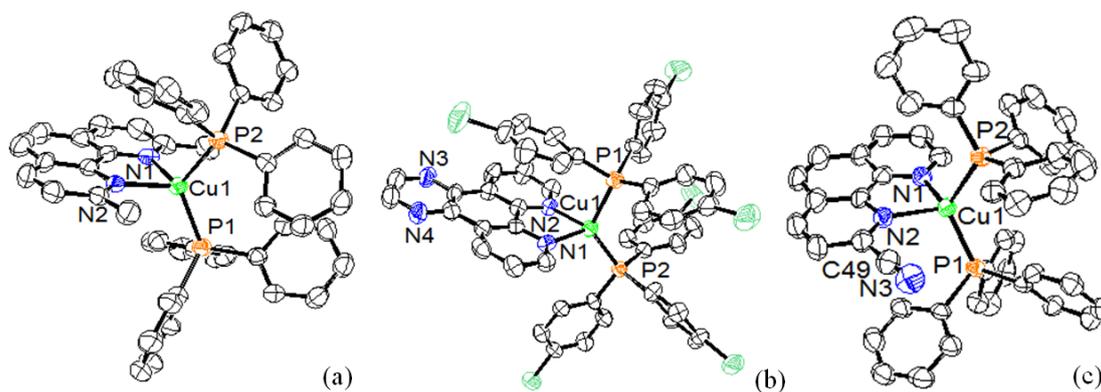


Figure 1. The cationic structures of (a) **2**, (b) **5c** and (c) **7**. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond parameters (Å, °) for **1**, **2**, **5c**, and **7**.

	2	5c	7
Cu–N1 (Å)	2.126(13)	2.078(6)	2.104(5)
Cu–N2 (Å)	2.128(13)	2.068(6)	2.082(5)
Cu–P1 (Å)	2.282(4)	2.274(2)	2.264(2)
Cu–P2 (Å)	2.284(4)	2.211(2)	2.267(2)
N1–Cu–N2 (°)	79.4(5)	80.5(2)	79.7(2)
P1–Cu–P2 (°)	123.6(16)	124.21(8)	123.57(7)

In addition to the above bonding environments, intramolecular π -stacking interactions are also observed for **2** and **5c**. In the structure of **2** (Figure S1), a phenyl ring of P(CIPh)₃ ligand exhibits intramolecular π -stacking with the central phenyl ring of **dpq** ligand with centroid-to-centroid distance of 3.65(1) Å, while the intramolecular π -stacking interaction arises between the phenyl rings of two different PPh₃ ligands for **2**. In contrast to **2** and **5c**, similar intramolecular π -stacking interaction is not observed in **7**, while extensive intermolecular π -stacking between the adjacent **phenCN** ligands, with the centroid-to-centroid distance of 4.05(2) Å, is found (Figure S2).

UV-vis Absorption Properties

The UV-vis absorption properties of these complexes have been investigated in CH₂Cl₂ solution. The overlaid absorption spectra are shown in Figure 2 and the absorption data are summarized in Table 2. All of these complexes (except **1**) show intense ligand-centered (LC) $\pi \rightarrow \pi^*$ absorptions of phosphine and diimine ligands with molar extinction coefficients on the order of $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in the UV region (220–290 nm). As with other Cu(I) diimine diphosphino complexes,^[15] these complexes also show ¹MLCT [d(Cu) \rightarrow $\pi^*(\text{N}-\text{N})$] transition at the lower energy region (340–410 nm). This assignment is supported by the dependence of the absorption energy on the electronic nature of the diimine ligands, which is in line with the energy level of π^* orbital of the diimine ligands for complexes containing the same phosphine ligands.^[16] In addition, the lowest energy absorptions of these complexes are sensitive to the nature of phosphine ligands. The increase of the π -accepting ability of the phosphine ligands [P(C₆H₄OMe)₃ < P(tol)₃ < PPh₃ < P(C₆H₄Cl)₃] results also in the blue-shift of the low-energy absorption for the complexes with the same diimine ligand [**5b** (407 nm) > **5a** (391 nm) > **5** (384 nm) > **5c** (377 nm)]. The increasing MLCT absorption energy of the complexes is probably *due* to the better stabilization of d(Cu)

orbital, as reflected by the anodically shifted metal-centered oxidation potentials (see below) in the presence of stronger π -accepting phosphine ligands.

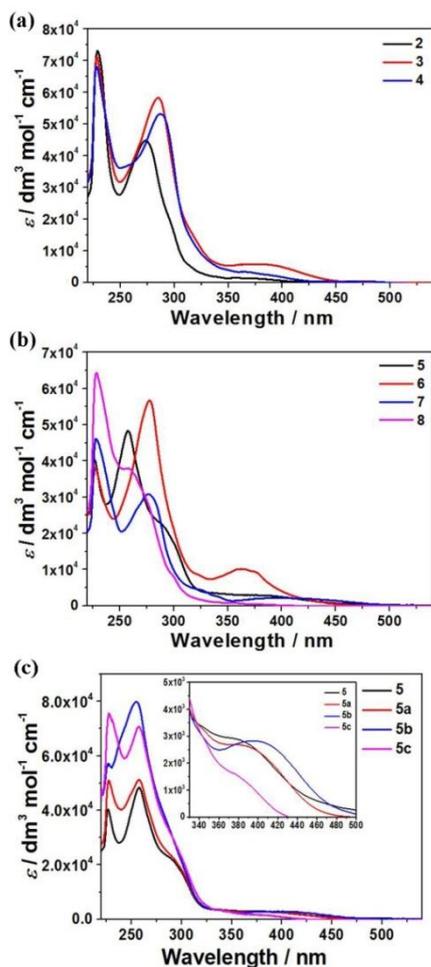


Figure 2. Overlaid UV/vis absorption spectra of (a) 2–4, (b) 5–8 and (c) 5, 5a–5c in CH_2Cl_2 solution.

Table 2. UV/vis absorption data of 1–8 in CH_2Cl_2 solution at 298 K.

	Absorption $\lambda_{\text{abs}} / \text{nm}$ ($\epsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)
1	227 (39290), 258(20900)
2	229 (73040), 274(44710), 373sh (1300)
3	228 (71180), 285 (58210), 381sh (5810)
4	228 (68830), 287 (53890), 369sh (3950)
5	226 (38620), 257 (48370), 384sh (2890)
5a	228 (50950), 258 (56390), 391sh (2600)
5b	227 (57060), 254 (79870), 407sh (2800)
5c	227 (75600), 258 (70700), 377sh (1620)
6	227 (38180), 277 (56690), 365 (10060)
7	227 (46090), 278 (30780), 403 (2090)
8	228 (64230), 258sh (37950), 370sh (3070)
8a	229 (84440), 264 (40660), 369sh (3800)
8b	231(78300), 266 (62200), 369sh (2950)

Emission Properties

Upon photo-excitation ($\lambda_{ex} = 420$ nm), these phosphine-containing Cu(I) diimine complexes (**2–8**) in CH_2Cl_2 solution at room temperature show yellow to red MLCT [$d(\text{Cu}) \rightarrow \pi^*(\text{N}-\text{N})$] phosphorescence with a structureless emission band peaking at 542–667 nm. The emission lifetimes are in the range of 0.02 to 27.6 μs . The emission data of the complexes are listed in Table 3 and the overlaid emission spectra of selected complexes are shown in Figure 3. Similar to the trend observed in the MLCT absorption energy of these complexes, their emission energy shows a trend consistent with the π -accepting ability of the diimine ligands [**8** (611 nm) > **3** (626 nm) > **5** (629 nm) > **7** (667 nm)] (Figure 3a).^[16] Among these complexes, **2** ($\lambda_{em} = 551$ nm) and **4** ($\lambda_{em} = 542$ nm) show the substantially higher emission energy in CH_2Cl_2 solution. This is ascribed to the steric effect of two methyl groups on the 2,9-positions of **phen**, which preclude the structural distortion on the excited state.^[17] The large geometry change of CT excited state *due* to the lack of sterically hindering substituents on the 2,9-positions of diimine ligands for other complexes is suggested by the large Stokes shift observed in their emission spectra. For **7** and **8**, which contain only one substituent on the α -position of the diimine ligands, the emission also exhibit larger Stokes shift as in those complexes with unsubstituted diimine ligands. The results reveal that the mono-substituted diimine ligand actually has negligible effect on precluding the structural distortion on the excited state.

By comparing the MLCT phosphorescence of complexes bearing varied phosphine ligands [**5**, **5a–5c** (Figure 3b) and **8**, **8a–8b**], but the same diimine ligand, it is noted that the emission energy not only varies with the electronic effect of the phosphine ligands but also with their steric properties. The introduction of both electron-donating and electron-withdrawing substituents in the phosphine ligands leads to a blue-shifted emission. This should be rationalized by following factors: (i) The electron-withdrawing Cl group on the phosphine ligands could lead to the blue-shifted emission, as it could stabilize the $d(\text{Cu})$ orbital and other occupied orbitals; (ii) It is well known that the structural rearrangement of Cu(I) complexes in their excited states typically leads to a red shift in emission which reduces the energy gap. The substitution of protons on the phosphine ligands by Cl or Me/MeO groups will result in the enhancement of the bulkiness in phosphine ligands and further inhibit the structural distortion in the excited state. Although the Me/MeO groups on the phosphine ligand will increase the energy level of HOMO, they could effectively inhibit the structural distortion in the excited state and thus result in higher energy emission. This factor will also result in the blue-shift of the luminescence.^[18] From the above variation trends, the steric effect is more pronounced than the electronic effect on the phosphine ligands. The more pronounced blue-shift is observed for **5c** as the electron-withdrawing Cl substituents have dual effects on its emission.

In solid state, these complexes show intense green to orange-red (519 to 629 nm) photoluminescence (Table 3, Figure 4). The intense solid emissions of these complexes are attributed to the decrease in the excited state distortion of Cu(I) complexes and non-radiative decay in solid state. Since the rigidochromic effect impedes the structural distortion in the excited state, the solid-state emissions for most of these Cu(I) complexes are blue-shifted relative to their solution emissions.^[19] In contrast to the solution emissions of these complexes, their solid emission show different variation trend on the electronic properties of phosphine ligands and diimine ligands. The deviation of the trend in their solid emission can be explained by the various factors such as inter- and inner-molecular π -stacking in these solid state, as similar to the previous solid emissions of related Cu(I) complexes.^[20,21] In 77 K EtOH-MeOH (4:1, v/v) glassy medium,

these complexes display intense luminescence (Figure 5 and Table 3). Except for **6**, these complexes show structureless emission bands. Compared with their solution emission, the emissions are generally blue-shifted and longer-lived. This is also attributed to the rigidochromic effect commonly observed in MLCT emitters.^[20,21] The submicrosecond excited state lifetimes in the glassy medium at 77 K further support the assignment of triplet excited state origin. These emissions are also tentatively assigned to be derived from $^3\text{MLCT}$ [$d(\text{Cu}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$] excited-state origin. The emission band of **6** in low-temperature glassy medium is highly structured with vibrational progression spacing of $\sim 1200\text{ cm}^{-1}$.^[22] The significant different emission characteristics of **6** is suggestive of a different emission origin at low temperature, which is ascribed to the ^3LC excited state origin of the **dppz** ligand.

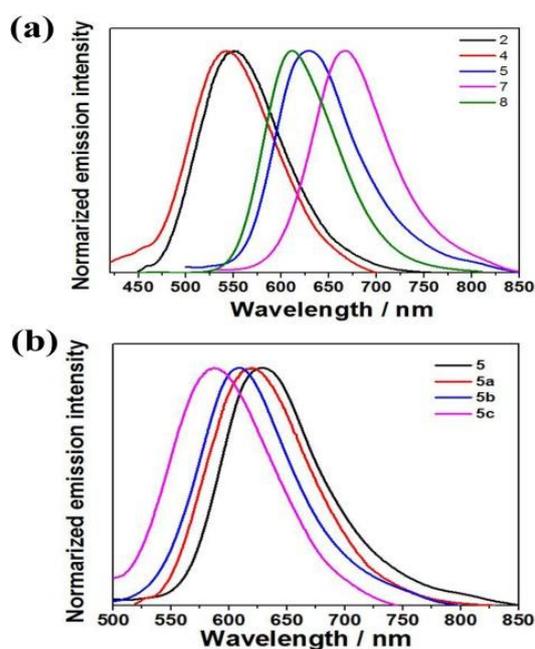


Figure 3. (a) Overlaid emission spectra of **2**, **4**, **5**, **7** and **8** in CH_2Cl_2 at room temperature; (b) Overlaid emission spectra of **5**, **5a**–**5c** in CH_2Cl_2 at room temperature.

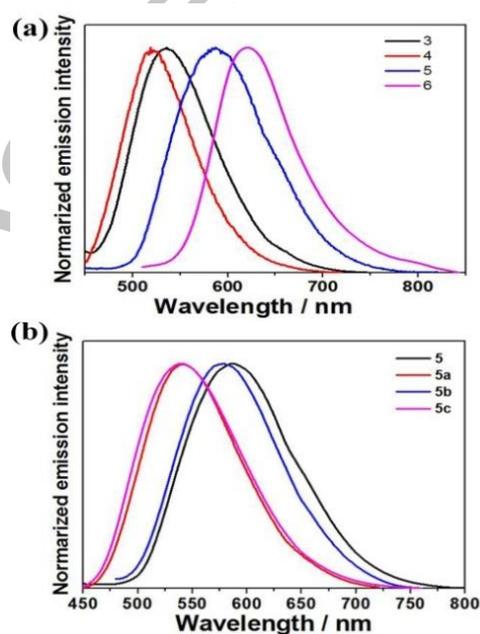


Figure 4. (a) Overlaid solid state emission spectra of **3**, **4**, **5** and **6** at room temperature; (b) Overlaid solid state emission spectra of **5**, **5a–5c** at room temperature.

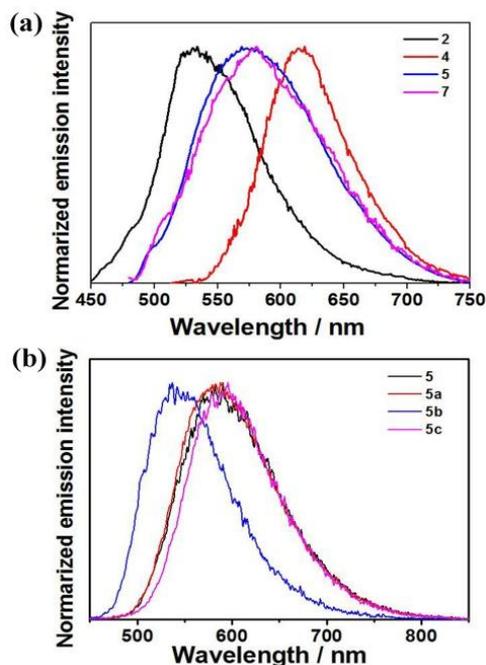


Figure 5. Overlaid emission spectra of **2**, **4**, **5** and **7** (a) and **5**, **5a–5c** (b) in glassy medium at 77 K.

Table 3. The emission data for compounds **3–8**.

	Medium (T / K)	Emission	$\phi_{em} (\times 10^3)^c$
		λ_{em}^a / nm ($\tau_c / \mu s$)	
(3)	CH ₂ Cl ₂ (298)	626 (0.2)	0.2
	Glass ^c (77)	535 (160.2)	
	Soild	536 (1.8)	
(4)	CH ₂ Cl ₂ (298)	542 (27.6)	146
	Glass ^c (77)	530 (282.5)	
	Soild	519 (10.1)	
(5)	CH ₂ Cl ₂ (298)	629 (0.1)	0.5
	Glass ^c (77)	569 (103.2)	
	Soild	587 (0.2)	
(5a)	CH ₂ Cl ₂ (298)	613 (0.02)	0.7
	Glass ^c (77)	569 (145.5)	
	Soild	537 (8.5)	
(5b)	CH ₂ Cl ₂ (298)	602 (0.02)	0.7
	Glass ^c (77)	575 (158.5)	
	Soild	582 (0.9)	
(5c)	CH ₂ Cl ₂ (298)	587 (0.03)	0.5
	Glass ^c (77)	582 (80.1)	
	Soild	541 (7.5)	
(6)	CH ₂ Cl ₂ (298)	620 (0.02)	0.5
	Glass ^c (77)	546, 590, 635 (0.29)	
	Soild	629 (0.12)	
(7)	CH ₂ Cl ₂ (298)	667 (0.37)	1.0
	Glass ^c (77)	577 (203.2)	
	Soild	588 (4.4)	
(8)	CH ₂ Cl ₂ (298)	611 (1.3)	6.4
	Glass ^c (77)	549 (146.1)	
	Soild	541 (5.9)	
(8a)	CH ₂ Cl ₂ (298)	605 (0.69)	5.6

	Glass ^c (77)	551 (195.2)	
	Soild	554 (5.6)	
(8b)	CH ₂ Cl ₂ (298)	603 (0.23)	2.9
	Glass ^c (77)	567 (213.4)	
	Soild	544 (11.4)	

Electrochemistry

The redox properties of the Cu(I) complexes in acetonitrile containing 0.1 M ⁿBuNPF₆ were recorded by cyclic voltammetry (CV) and the corresponding electrochemical data were summarized in Table 4. Representative CVs of these complexes are shown in Figure 6. Complex **1** shows an irreversible metal-centered oxidation potential at $E_{pa} = 0.31$ V (vs Cp₂Fe⁺⁰). Except for **2** and **4**, all the complexes showed an irreversible oxidation wave with E_{pa} in the range of +0.85 to +1.05 V vs Cp₂Fe⁺⁰, which are comparable with those commonly observed in the Cu(I) diimine complex systems. They are assigned to metal-centered Cu^{II/I} oxidation. Such an assignment is supported by the dependence of the potential on the substituents and π -conjugating effects of the diimine ligand, similar to those reported in the related complexes.^[3,4] In general, a higher oxidation potential is observed for complex bearing phosphine and diimine ligands of stronger π -accepting properties, which better stabilize the d(Cu) orbital. The influence of the substituents on the phosphine ligands towards the metal-centered oxidation is more significant than that of the diimine ligands. An investigation of complexes with the same diimine ligand but different phosphine ligands shows that the positions of oxidation couples are in line with the π -accepting ability of the phosphine ligands, which is in the order **5c** (+1.05 V) > **5** (+0.87 V) > **5a** (+0.73 V) > **5b** (+0.49 V).

In the reduction scan, except for **8**, **8a** and **8b**, these complexes all show a reversible reduction couple at *approx.* -2 V vs. Cp₂Fe⁺⁰. The high sensitivity of the reduction potential to the electronic nature of diimine ligand is suggestive of the ligand-centered reduction.^[16]

Table 4. Electrochemical data with 0.1 M [ⁿBu₄N]PF₆ in MeCN at 298 K.^a

	Oxidation E_{pa} (vs. Fc ⁺⁰) [V] ^b	Reduction $E_{1/2}$ or E_{pa} (vs. Fc ⁺⁰) [V] ^b (ΔE_p [mV]) ^c
1	0.31	/
2	0.63	-2.07(64)
3	0.85	-1.92(71)
4	0.61	-2.00(69)
5	0.87	-1.84(60)
5a	0.73	-1.85(68)
5b	0.49	-1.86(72)
5c	1.05	-1.82(94)
6	0.88	-1.45(64)
7	0.85	-1.57(56)
8	0.89	-1.86
8a	0.78	-2.09
8b	0.77	-2.07

^a Working electrode: glassy carbon; scan rate, 100 mV s⁻¹. ^b $E_{1/2}$ is $(E_{pa} + E_{pc})/2$ and $\Delta E_p = |E_{pa} - E_{pc}|$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively.^c

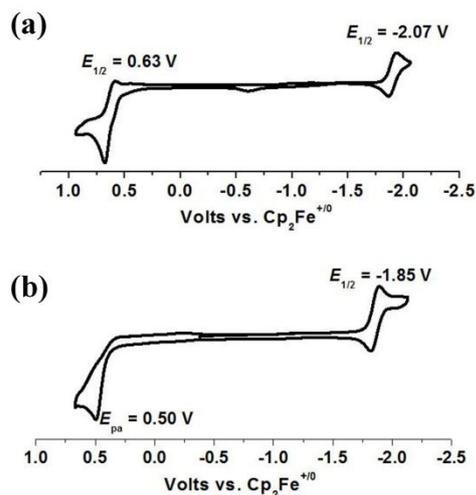


Figure 6. Cyclic voltammograms of (a) **2** and (b) **5c** in 0.1 M [ⁿBu₄N]PF₆ MeCN solution with scan rate = 100 mVs⁻¹.

Conclusions

We have studied a new series of luminescent Cu(I) diimine phosphino complexes. These complexes exhibit MLCT phosphorescence with emission energy, lifetimes and quantum yields strongly dependence on the nature of the diimine and phosphine ligands. It is worth to note that both the electronic and steric effects of substituting groups in phosphine ligands affect significantly the emission properties of these complexes. Our work should provide structural-properties information for the future design of luminescent Cu(I) complexes.

Experimental

Materials and reagents

2,9-Dimethyl-1,10-phenanthroline (**dmp**), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (**Ph₂dmp**) and 4,7-diphenyl-1,10-phenanthroline (**Ph₂phen**) were purchased from Acros Organic Chemical Company. Triphenylphosphine (**PPh₃**), tri(*p*-tolyl)phosphine [**P(MePh)₃**], tri(4-methoxyphenyl)phosphine [**P(MeOPh)₃**] and tri(4-chlorophenyl)phosphine [**P(ClPh)₃**] were purchased from Strem Chemical Company. These commercially available reagents were used without further purification. 2-Hydroxyl-1,10-phenanthroline (**phenOH**),^[23] 2-cyano-1,10-phenanthroline (**phenCN**),^[24] dipyrido[3,2-d:2',3'-f]quinoxaline (**dpq**),^[25] dipyridophenazine (**dppz**),^[11] and the complexes [Cu(MeCN)₄](ClO₄) (**1**)^[12] and [Cu(PPh₃)₂(**dmp**)](ClO₄) (**2**)^[26] were synthesized according to literature procedures. All other reagents and solvents were of analytical grade and were used without further purification.

Synthesis

All reactions were carried out under strictly anaerobic conditions under an inert argon atmosphere by using standard Schlenk techniques.

[Cu^I(PPh₃)₂(Ph₂Phen)](ClO₄) (3) [Cu^I(MeCN)₄](ClO₄) (50 mg, 0.15 mmol), PPh₃ (80.4 mg, 0.30 mmol) and **Ph₂Phen** (55.9 mg, 0.17 mmol) in MeCN (15 ml) are stirred at room temperature for 1 h. Slow evaporation of a MeCN solution of **3** afforded analytically pure complex as yellow crystalline solid. Yield (93.1 mg, 59.8 %). Elemental analysis for C₆₀H₄₆ClCuN₂O₄P₂: *calcd.* C 70.65, H 4.55, N 2.75%; *found:* C 70.60, H 4.70, N 2.77%. Selected IR (KBr, cm⁻¹): ν(Cl-O) 1111. ESI-MS (positive): *m/z* 919 (*M*⁺). ¹H NMR (300 MHz, CDCl₃): δ 8.83 (d, *J* = 5.0 Hz, 2H, phen H); 8.01 (s, 2H, phen H); 7.74 (d, *J* = 5.0 Hz, 2H, phen H); 7.62 (m, 6H, phenyl H); 7.57–7.51 (m, 4H, phenyl H); 7.37 (m, 6H, phenyl H); 7.26–7.14 (m, 24H, phenyl H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 2.97 (s, PPh₃). UV/Vis (CH₃CN): λ_{max}/nm (ε /mol⁻¹ dm³ cm⁻¹): 228 (71180), 285 (58210), 381 sh (5810).

[Cu^I(PPh₃)₂(Ph₂dmp)](ClO₄) (4) [Cu^I(MeCN)₄](ClO₄) (50mg, 0.15 mmol), PPh₃ (80.4 mg, 0.30 mmol) and **Ph₂dmp** (60.7 mg, 0.18 mmol) in MeCN (15 ml) are stirred at room temperature for 1 h. Slow evaporation of a MeCN solution of **4** afforded analytically pure complex as yellow crystalline solid. Yield (93.4 mg, 62.9 %). Elemental analysis for C₆₂H₅₀ClCuN₂O₄P₂: *calcd.* C 71.06, H 4.81, N 2.67%; *found:* C 71.12, H 4.90, N 2.62%. Selected IR (KBr, cm⁻¹): ν(Cl-O) 1110. ESI-MS (positive): *m/z* 947 (*M*⁺). ¹H NMR (300 MHz, CDCl₃): δ 7.98 (s, 2H, Phen H); 7.60 (m, 6H, phenyl H); 7.57–7.53 (m, 4H, phenyl H); 7.44 (s, 2H, phen H); 7.38–7.42 (m, 6H, phenyl H); 7.26–7.21 (m, 24H, phenyl H); 2.31 (s, 6H, -CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 0.87 (s, PPh₃). UV/Vis (CH₃CN): λ_{max} /nm (ε /mol⁻¹ dm³ cm⁻¹): 228 (68830), 287 (53890), 369 sh (3950).

[Cu^I(PPh₃)₂(dpq)](ClO₄) (5) [Cu^I(MeCN)₄](ClO₄) (50 mg, 0.15 mmol), PPh₃ (80.4 mg, 0.30 mmol) and **dpq** (39.0 mg, 0.18 mmol) in MeCN (15 ml) are stirred at room temperature for 1 h. Recrystallization by slow diffusion of diethyl ether into a CH₂Cl₂ solution of **5** afforded analytically pure complex as yellow crystalline solid. Yield (88.4 mg, 62.9 %). Elemental analysis for C₅₀H₃₈ClCuN₄O₄P₂: *calcd.* C 65.29, H 4.16, N 6.09%; *found:* C 65.27, H 4.22, N 6.04%. Selected IR (KBr, cm⁻¹): ν(Cl-O) 1093. ESI-MS (positive): *m/z* 819 (*M*⁺). ¹H NMR (300 MHz, CDCl₃): δ 9.63 (d, *J* = 8.1 Hz, 2H, dpq H); 8.90 (s, 2H, dpq H); 8.03 (d, *J* = 7.7 Hz, 2H, dpq H); 7.31–7.36 (m, 6H, phenyl H); 7.13–7.23 (m, 24H, phenyl H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 2.50 (s, PPh₃). UV/Vis (CH₃CN): λ_{max} /nm (ε /mol⁻¹ dm³ cm⁻¹): 226 (40320), 257 (48370), 384 sh (2890).

[Cu^I{P(PhMe)₃}₂(dpq)](ClO₄) (5a) [Cu^I(MeCN)₄](ClO₄) (50 mg, 0.15 mmol), P(PhMe)₃ (93.1 mg, 0.30 mmol) and **dpq** (39.0 mg, 0.18 mmol) in MeCN (15 ml) are stirred at room temperature for 1 h. Recrystallization by slow diffusion of diethyl ether into a CH₂Cl₂ solution of **5a** afforded analytically pure complex as yellow crystalline solid. Yield (80.2 mg, 52.3 %). Elemental analysis for C₅₆H₅₀ClCuN₄O₄P₂: *calcd.* C 66.99, H 5.02, N 5.58%; *found:* C 66.80, H 5.13, N 5.60%. Selected IR (KBr, cm⁻¹): ν(Cl-O) 1094. ESI-MS (positive): *m/z* 903 (*M*⁺). ¹H NMR (300 MHz, CDCl₃): δ 9.61 (d, *J* = 7.3 Hz, 2H, dpq H); 9.15 (s, 2H, dpq H); 8.87 (s, 2H, dqp H); 8.01 (dd, *J* = 8.1, 4.9 Hz, 2H, dpq H); 7.13–6.89 (m, 24H, phenyl H); 2.28 (s, 18H, -CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 2.39 (s, PPh₃). UV/Vis (CH₃CN): λ_{max} /nm (ε /mol⁻¹ dm³ cm⁻¹): 228 (73590), 258 (56390), 391 sh (2600).

[Cu^I{P(PhOMe)₃}₂(dpq)](ClO₄) (5b) [Cu^I(MeCN)₄](ClO₄) (50 mg, 0.15 mmol), P(MeOPh)₃ (107.8 mg, 0.30 mmol) and **dpq** (39.0 mg, 0.18 mmol) in MeCN (15 ml) are stirred at room temperature for 1 h. Recrystallization by slow diffusion of diethyl ether into a CH₂Cl₂ solution of **5b** afforded analytically pure complex as yellow crystalline solid. Yield (82.3 mg, 48.9 %). Elemental analysis for C₅₆H₅₀ClCuN₄O₁₀P₂: *calcd.* C 61.15, H 4.58, N 5.09%; *found:* C 61.05, H

4.62, N 5.01%. Selected IR (KBr, cm^{-1}): $\nu(\text{Cl-O})$ 1097. ESI-MS (positive): m/z 999 (M^+). ^1H NMR (300 MHz, CDCl_3): δ 9.59 (dd, $J = 8.2, 1.3$ Hz, 2H, dpq H); 9.13 (s, 2H, dpq H); 8.97 (d, $J = 4.3$ Hz, 2H, dpq H); 8.05 (dd, $J = 8.2, 4.8$ Hz, 2H, dpq H); 7.07 (d, $J = 8.2$ Hz, 12H, phenyl H); 6.71 (d, $J = 8.7$ Hz, 12H, phenyl H); 3.76 (s, 18H, -OMe H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 0.36 (s, PPh_3). UV/Vis (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$): 227 (57060), 254 (79870), 407 sh (2800).

[Cu^I{P(PhCl)₃]₂(dpq)](ClO₄) (5c) $[\text{Cu}^{\text{I}}(\text{MeCN})_4](\text{ClO}_4)$ (50 mg, 0.15 mmol), $\text{P}(\text{PhCl})_3$ (111.1 mg, 0.30 mmol) and **dpq** (39.0 mg, 0.18 mmol) in MeCN (15 ml) are stirred at room temperature for 1 h. Slow evaporation of a MeCN solution of **5c** afforded analytically pure complex as yellow crystalline solid. Yield (90.7 mg, 52.8 %). Elemental analysis for $\text{C}_{50}\text{H}_{32}\text{Cl}_7\text{CuN}_4\text{O}_4\text{P}_2$: *calcd.* C 53.31, H 2.81, N 4.97%; found: C 53.35, H 2.95, N 4.89%. Selected IR (KBr, cm^{-1}): $\nu(\text{Cl-O})$ 1110. ESI-MS (positive): m/z 1023 (M^+). ^1H NMR (300 MHz, CDCl_3): δ 9.64 (d, $J = 8.1$ Hz, 2H, dqp H); 9.16 (s, 2H, dpq H); 9.10 (d, $J = 4.0$ Hz, 2H, dpq H); 8.13 (dd, $J = 8.2, 4.7$ Hz, 2H, dpq H); 7.24–7.26 (m, 12H, phenyl H); 7.07–7.12 (m, 12H, phenyl H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 0.36 (s, PPh_3). UV/Vis (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$): 227 (75600), 258 (70700), 377 sh (1620).

[Cu^I(PPh₃)₂(dppz)](ClO₄) (6) $[\text{Cu}^{\text{I}}(\text{MeCN})_4](\text{ClO}_4)$ (50 mg, 0.15 mmol), PPh_3 (80.4 mg, 0.30 mmol) and **dppz** (47.5 mg, 0.18 mmol) in MeCN (15 ml) are stirred at room temperature for 1 h. Slow evaporation of a MeCN solution of **6** afforded analytically pure complex as yellow crystalline solid. Yield (80.3 mg, 50.6 %). Elemental analysis for $\text{C}_{54}\text{H}_{40}\text{ClCuN}_4\text{O}_4\text{P}_2$: *calcd.* C 66.87, H 4.16, N 5.78%; found: C 66.80, H 4.20, N 5.75%. Selected IR (KBr, cm^{-1}): $\nu(\text{Cl-O})$ 1094. ESI-MS (positive): m/z 792 (M^+). ^1H NMR (300 MHz, CDCl_3): δ 9.76 (dd, $J = 8.2, 1.5$ Hz, 2H, dppz H); 8.88 (dd, $J = 4.9, 1.5$ Hz, 2H, dppz H); 8.45 (dd, $J = 6.6, 3.4$ Hz, 2H, dppz H); 8.11–7.98 (m, 4H, dppz H); 7.39–7.30 (m, 6H, phenyl H); 7.25–7.08 (m, 24H, phenyl H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 3.58 (s, PPh_3). UV/Vis (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$): 227 (38180), 277 (56694), 362 (10190).

[Cu^I(PPh₃)₂(PhenCN)](ClO₄) (7) $[\text{Cu}^{\text{I}}(\text{MeCN})_4](\text{ClO}_4)$ (50 mg, 0.15 mmol), PPh_3 (80.4 mg, 0.30 mmol) and **phenCN** (34.5 mg, 0.18 mmol) in MeCN (15 ml) are stirred at room temperature for 1 h. Recrystallization by slow diffusion of diethyl ether into a CH_2Cl_2 solution of **7** afforded analytically pure complex as yellow crystalline solid. Yield (89.4 mg, 65.6 %). Elemental analysis for $\text{C}_{49}\text{H}_{37}\text{ClCuN}_3\text{O}_4\text{P}_2$: *calcd.* C 65.92, H 4.18, N 4.71%; found: C 65.99, H 4.20, N 4.78%. Selected IR (KBr, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 1969; $\nu(\text{Cl-O})$ 1111. ESI-MS (positive): m/z 792 (M^+). ^1H NMR (300 MHz, CDCl_3): δ 8.90 (d, $J = 8.3$ Hz, 1H, phenCN H); 8.74–8.66 (m, 1H, phenCN H); 8.31 (q, $J = 9.0$ Hz, 2H, phenCN H); 8.22 (s, 1H, phenCN H); 8.00 (d, $J = 8.3$ Hz, 1H, phenCN H); 7.76 (dd, $J = 8.0, 4.7$ Hz, 1H, phenCN H); 7.42–7.32 (m, 6H, phenyl H); 7.24–7.05 (m, 24H, phenyl H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 3.56 (s, PPh_3). UV/Vis (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$): 227 (46090), 278 (30780), 403 (2090).

[Cu^I(PPh₃)₂(phenOH)](ClO₄) (8) $[\text{Cu}^{\text{I}}(\text{MeCN})_4](\text{ClO}_4)$ (50 mg, 0.15 mmol), PPh_3 (80.4 mg, 0.30 mmol) and **phenOH** (33.2 mg, 0.18 mmol) in MeCN (15 ml) are stirred at room temperature for 1 h. Slow evaporation of a MeCN solution of **8** afforded analytically pure complex as yellow crystalline solid. Yield (79.4 mg, 58.8 %). Elemental analysis for $\text{C}_{48}\text{H}_{38}\text{ClCuN}_2\text{O}_5\text{P}_2$: *calcd.* C 65.23, H 4.33, N 3.17%; found: C 65.20, H 4.42, N 3.20%. Selected IR (KBr, cm^{-1}): $\nu(\text{Cl-O})$ 1094. ESI-MS (positive): m/z 867 (M^+). ^1H NMR (300 MHz, CDCl_3): δ 10.70 (s, 1H, -OH H); 8.33 (d, $J = 8.2$ Hz, 1H, phen H); 8.28 (d, $J = 3.5$ Hz, 1H, phen H); 8.20 (d, $J = 8.9$ Hz, 1H, phen H); 7.86 (d,

$J = 8.8$ Hz, 1H, phen H); 7.72 (d, $J = 8.8$ Hz, 1H, phen H); 7.65 (d, $J = 9.1$ Hz, 1H, phen H); 7.48 (dd, $J = 8.1, 4.7$ Hz, 1H); 7.35–7.43 (m, 6 H, phenyl H); 7.17–7.27 (m, 24 H, phenyl H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 0.08 (s, PPh_3). UV/Vis (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$): 228 (64230), 258 sh (37950), 370 sh (3070).

[Cu^I{P(PhMe)₃}₂(phenOH)](ClO₄) (8a) [$\text{Cu}^{\text{I}}(\text{MeCN})_4(\text{ClO}_4)$] (50 mg, 0.15 mmol), $\text{P}(\text{PhMe})_3$ (93.1 mg, 0.30 mmol) and **phenOH** (33.2 mg, 0.18 mmol) in MeCN (15 ml) are stirred at room temperature for 1 h. Slow evaporation of a MeCN solution of **8a** afforded analytically pure complex as yellow crystalline solid. Yield (73.5 mg, 49.7 %). Elemental analysis for $\text{C}_{54}\text{H}_{50}\text{ClCuN}_2\text{O}_5\text{P}_2$: *calcd.* C 67.01, H 5.21, N 2.89%; found: C 67.10, H 5.23, N 2.94%. Selected IR (KBr, cm^{-1}): $\nu(\text{Cl-O})$ 1094. ESI-MS (positive): m/z 867 (M^+). ^1H NMR (300 MHz, CDCl_3): δ 10.61 (s, 1H, -OH H); 8.31 (s, 1H, phen H); 8.29 (d, $J = 2.0$ Hz, 1H, phen H); 8.18 (d, $J = 8.8$ Hz, 1H, phen H); 7.82 (d, $J = 8.8$ Hz, 1H, phen H); 7.67 (dd, $J = 12.5, 9.4$ Hz, 1H, phen H); 7.55 (dd, $J = 11.8, 8.1$ Hz, 1H, phen H); 7.47 (dd, $J = 7.4, 5.4$ Hz, 1H, phen H); 7.02–7.08 (m, 12 H, phenyl H); 6.91–6.95 (m, 12 H, phenyl H); 2.30 (s, 18H, -CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 0.36 (s, PPh_3). UV/Vis (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$): 229 (84440), 264 (40660), 369 sh (3800).

[Cu^I{P(PhOMe)₃}₂(phenOH)](ClO₄) (8b) [$\text{Cu}^{\text{I}}(\text{MeCN})_4(\text{ClO}_4)$] (50 mg, 0.15 mmol), $\text{P}(\text{PhOMe})_3$ (107.8 mg, 0.30 mmol) and **phenOH** (33.2 mg, 0.18 mmol) in MeCN (15 ml) are stirred at room temperature for 1 h. Slow evaporation of a MeCN solution of **8b** afforded analytically pure complex as yellow crystalline solid. Yield (76.2 mg, 46.9%). Elemental analysis for $\text{C}_{54}\text{H}_{50}\text{ClCuN}_2\text{O}_{11}\text{P}_2$: *calcd.* C 60.96, H 4.74, N 2.63%; found: C 60.75, H 4.79, N 2.56%. Selected IR (KBr, cm^{-1}): $\nu(\text{Cl-O})$ 1097. ESI-MS (positive): m/z 963 (M^+). ^1H NMR (300 MHz, CDCl_3): δ 10.59 (s, 1H, -OH H); 8.41–8.35 (m, 1H, phen H); 8.32 (dd, $J = 8.2, 1.3$ Hz, 1H, phen H); 8.18 (d, $J = 8.5$ Hz, 1H, phen H); 7.83 (d, $J = 8.8$ Hz, 1H, phen H); 7.71 (d, $J = 8.8$ Hz, 1H, phen H); 7.59 (dd, $J = 13.0, 4.3$ Hz, 1H, phen H); 7.51 (dd, $J = 8.1, 4.7$ Hz, 1H, phen H); 7.09 (d, $J = 7.7$ Hz, 12H, phenyl H); 6.67 (d, $J = 8.6$ Hz, 12H, phenyl H); 3.78 (s, 18H, -CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 0.87 (s, PPh_3). UV/Vis (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$): 231(78300), 266 (62200), 369 sh (2950).

Physical measurements and instrumentation

^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AV300 (300 MHz) FT-NMR spectrometer. Chemical shifts (δ , ppm) are reported relative to tetramethylsilane (Me_4Si). All positive-ion ESI mass spectra were recorded on a PE-SCIEX API 150 EX single-quadrupole mass spectrometer. Elemental analysis was performed on an Elementar Vario MICRO Cube elemental analyzer. IR spectra of the solid samples as KBr discs were obtained within the range 4000–400 cm^{-1} on an AVATAR 360 FTIR spectrometer. All of the electronic absorption spectra were recorded on a Hewlett–Packard 8453 or Hewlett–Packard 8452A diode-array spectrophotometer. Steady-state emission spectra were measured at RT and at 77 K on a Horiba JobinYvon Fluorolog-3-TCSPC spectrofluorometer. The solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with not less than four successive freeze–pump–thaw cycles. The measurements at 77 K were carried out on dilute solutions of the samples in EtOH/MeOH (4:1 v/v) loaded in a quartz tube inside a quartz-walled Dewar flask that contained liquid nitrogen. Luminescence quantum yields were determined using the optical dilution method described by Demas and Crosby^[27] with an aqueous solution of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ ($\phi_{\text{em}} = 0.042$)^[28]

with 436 nm excitation) at room temperature as reference. Luminescence lifetimes were measured by using the time-correlated single-photon-counting (TCSPC) technique on a Fluorolog-3-TCSPC spectrofluorometer in a fast MCS mode with a Nano LED-375 LH excitation source, which had a peak excitation wavelength at 375 nm and a pulse width of less than 750 ps. The photon-counting data were analyzed on Horiba Jobin Yvon Decay Analysis Software.

Cyclic Voltammetry (CV)

Measurements were performed on a CH Instruments, Inc. Model CHI 620 Electrochemical Analyzer. Electrochemical measurements were performed in MeCN solution with [ⁿBu₄N]PF₆ (0.1M) as a supporting electrolyte at room temperature. The reference electrode was Ag/AgCl (0.1M in MeCN) electrode and the working electrode was a glassy carbon electrode (CH Instruments, Inc.) with platinum wire as the counter electrode. The surface of the working electrode was polished with a 1 μm *α*-alumina slurry (Linde) and then with a 0.3 μm *α*-alumina slurry (Linde) on a microcloth (Buehler Co.). The ferrocenium/ferrocene⁺⁰ couple (FeCp₂⁺⁰) was used as an internal reference. All of the solutions for the electrochemical studies were de-aerated with pre-purified argon gas prior to the measurements.

X-ray Crystal Structure Determination

The crystal structures were determined on an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer by using graphite-monochromated Cu-K_α radiation ($\lambda = 1.5417 \text{ \AA}$). The structures were solved by using direct methods with the SHELXS-97 program.^[29] The Ru atoms and many of the non-hydrogen atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were located after refinement by full-matrix least-squares by using the SHELXL-97 program.^[30] In the final stage of the least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by using the SHELXL-97 program. The positions of H atoms were calculated based on the riding model with thermal parameters that were 1.2 times that of the associated C atoms and participated in the calculation of the final R indices. CCDC-1498290 (**2**), 1498291 (**5c**), and 1498292 (**7**) 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.

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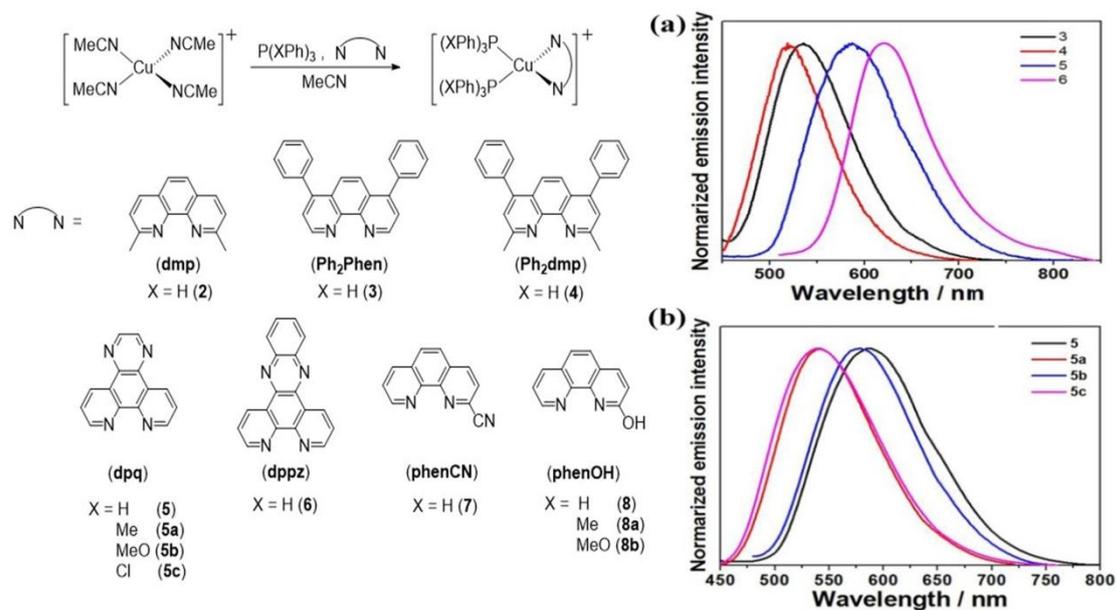
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A series of luminescent Cu(I) complexes bearing various diimine and phosphine ligands have been obtained and their luminescent properties are significantly influenced by the nature of diimine and PPh₃ ligands.