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Syntheses, structures and photophysical properties of a series of luminescent copper(I) mixed-ligand complexes

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ABSTRACT

The reaction of $[Cu(NCCH_3)_4]ClO_4$ with a chelating diimine ligand and 1,2-bis(diphenylphosphane)benzene (bdpp) in dichloromethane solution gives good yields of a series of mixed-ligand copper(1) complexes $[Cu(diimine)(bdpp)]ClO_4$, where the diimine ligands are 2,2'-bipyridine (bpy), 5,5'-dibromo-2,2'-bipyridine (BrbpyBr), 5,5'-diethynyl-2,2'-bipyridine (HC=CbpyC=CH), 1,10-phenanthroline (phen) and 3,8dibromo-1,10-phenanthroline (BrphenBr) in complexes **1–5**, respectively. All the structures are confirmed by single crystal X-ray structure analysis. A study of the HRMS results suggest that the [Cu(diimine)(bdpp)]⁺ cations for complexes **1–5** are kinetically stable products, and [Cu(bdpp)₂]⁺ is the thermodynamically stable product in DCM solution. In the crystal structures of complexes **1–5**, $\pi \cdots \pi$ and $C-H \cdots \pi$ interactions widely exist, among which **4**·CH₂Cl₂ shows the most striking example. The triple $\pi \cdots \pi$ interactions within the cation dimer and the rich $C-H \cdots \pi$ interactions among the cation dimers are suggested to be the main reasons of the high emissive quantum yield of 18.33% in the solid state under air for complex **4**.

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1. Introduction

Complexes of the Cu(I) ion have received more and more attention [1,2] in the construction of luminescent materials and for the development of practical components for chemical sensors, display devices and solar-energy conversion schemes due to their abundant resource, comparatively low cost and non-toxic properties compared to noble metals systems such as Re(I) [3], Ir(III) [4], Pt(II) [5] and Au(I) [6]. Among the luminescent copper(I) systems, the mixed-ligand copper(I) complexes [Cu(diimine)(PP)]⁺ (PP = chelating diphosphane ligand), which contain one diimine ligand such as 1.10-phenanthroline (phen) or 2.2'-bipyridine (bpy) and one chelating diphosphane ligand, have been the object of intense investigations due to their enhanced luminescent performance [1a,f,7] and considerably increased lifetimes of the triplet states relative to the corresponding $[Cu(diimine)_2]^+$ complexes [8,1f]. It is reported that the [Cu(phen)(PP)]⁺ complexes are more similar to the well luminescent ruthenium(II) polypyridine complexes than to their copper(I) bis(phenanthroline) analogs when considering the electronic and photophysical properties [7b,9].

On the other hand, it is well known that when the bulky substituents are close to the donor atoms, the steric crowding in the

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coordination shell would suppress ligand-addition reactions and inhibit the flattening distortion in the excited state, and hence solvent-induced quenching by an exciplex mechanism would be impeded [7a,10] and an obvious increase in the emissive quantum yield can be expected. Following such a consideration, most reports have focused their interest on the introduction of a bulky substituent of the phenanthroline ligand at the 2- and 9-positions into the coordination sphere. But increasing the bulk of the substituent in the coordination sphere would also increase the repulsion between the diimine and diphosphane ligands, and hence decrease the stability of the Cu(I) complexes. It is well known that phosphorescence enhancement widely exists for the [Cu(diimine)(PP)]⁺ complexes in the solid state because of the $\pi \cdots \pi$ interaction between the diimine ligands [1c]. The bulky substituent would also weaken the $\pi \cdots \pi$ interaction and the emission in the solid state. To the best of our knowledge, few reports exist on the change of the 3- and 8-positions of phen or 5- and 5'-positions of bpy, but such changes can lead to a change in the conjugacy of these diimine ligands. Past work has shown that increasing delocalization within the π system of a diimine ligand can alter the nature of the lowest excited state in these complexes and enhance the lifetime [11]. Furthermore, introduction of bromine atoms into these positions of the diimine ligands may enhance the phosphorescence emission due to the heavy atom effect of the bromine atoms and hence lead to a longer emission lifetime compared with the fluorescent systems.





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In order to reach a better understanding of the effects of the conjugacy of the diimine ligands, the heavy atoms effect and $\pi \cdots \pi$ interactions on photophysical properties, a series of diimine ligands, by changing the substituents at the 5- and 5'-positions of bpy or 3- and 8-positions of phen, are used in this article. Here, a series of mononuclear mixed-ligand [Cu(diimine)(bdpp)]ClO₄ complexes **1–5** were obtained (diimine = bpy **1**, 5,5'-dibromo-2,2'-bipyridine (BrbpyBr) **2**, 5,5'-diethynyl-2,2'-bipyridine (HC) CbpyC) CH) **3**, phen **4** and 3,8-dibromo-1,10-phenanthroline (BrphenBr) **5**, bdpp = 1,2-bis(diphenylphosphane)benzene), and their structures and photophysical properties in the solid state are reported.

2. Results and discussion

2.1. Syntheses

Complexes **1–5** (Scheme 1) were obtained in good yields by the reaction of an equimolar ratio of $Cu(CH_3CN)_4ClO_4$, chelating diimine and bdpp ligands as a stirred dichloromethane (DCM) solution or DCM/CH₃CN (1:1) solution. Complex **1** crystallizes without any solvent. Unlike complex **1**, complexes **2–5** crystallize as their 1:1 dichloromethane solvates. All the complexes are stable to air and moisture in the solid state. It is well accepted that the P atom is a more soft donor than the N atom, hence it is suitable for stabilizing the soft Lewis acid Cu(I) ion according to HSAB rules [12]. Therefore in most cases, as a result, it was found that the stable [Cu(diimine)(PP)]⁺ complexes rather than their corresponding [Cu(diimine)₂]⁺ complexes were formed in the mixed-ligand systems. However, an effort to synthesize [Cu(dmp)(bdpp)]ClO₄

(dmp = 2,9-dimethyl-1,10-phenanthroline) was not found to be successful, as for complexes 1-5 and those reported analogs $[Cu(dppe)(dmp)]PF_6$ (dppe = 1,2-bis(diphenylphosphino)ethane) and $[Cu(dppp)(dmp)]PF_6$ (dppp = 1,3-bis(diphenylphosphino)propane) [8c]. Layering *n*-hexane onto the corresponding DCM solution gave only one product as red crystals, which was identified as $[Cu(dmp)_2]ClO_4$ by HRMS, with a cation peak at m/z 479.135. This significant difference may arise from the repulsion between the dmp and bdpp ligands since the two methyl groups in dmp are close to the N donor atoms and the phenyl rings connected to the P atoms are more crowded in bdpp than in dppp and dppe due to the rigidity of the central phenyl ring of bdpp. On the other hand, the failure to isolate [Cu(dmp)(bdpp)]ClO₄ may also be due to kinetic effects of crystallization since an equilibrium of different species is likely in the solution. It is worth noting that it was reported by Armaroli's group that the reaction of $[Cu(CH_3CN)_4]BF_4$ with a 1:1 mixture of phen and bdpp also did not give the expected mononuclear $[Cu(phen)(bdpp)]BF_4$ complex, instead $[Cu(bdpp)_2]$ BF₄ was obtained [13]. This difference was explained speculatively by the different bite angles for the different chelating diphosphane ligands. When this angle (such as in bdpp) is small enough, the metal center can easily accommodate two diphosphanes ligands. In contrast, steric factors resulting from the wider P-Cu-P angles for the other chelating diphosphanes substantially destabilizes the $[Cu(PP)_2]^+$ derivatives, thus preventing their formation [13]. However, here the reaction of [Cu(CH₃CN)₄]ClO₄ with a 1:1 mixture of phen or BrphenBr and bdpp gave the corresponding mononuclear [Cu(diimine)(bdpp)]ClO₄ complexes rather than the complex [Cu(bdpp)₂]ClO₄. It should be noted that when diluted solutions of complexes 1-5, with concentrations of ca. $1.0\times 10^{-5}\,mol\,L^{-1},$ were left for a long enough time, such as a



Scheme 1. Synthetic routes to complexes 1-5.

month, the color of the solutions were found to become nearly colorless and $[Cu(bdpp)_2]^+$ ions were found to be the main species identified by the HRMS results, with a cation peak at m/z 955.200, suggesting that the $[Cu(diimine)(bdpp)]^+$ cations for complexes **1–5** are kinetically stable products and $[Cu(bdpp)_2]^+$ is the thermodynamically stable product in DCM solution.

2.2. Crystallographic studies

The crystal structures of all the complexes have been determined by single crystal X-ray diffraction. Complexes **1**, **2**·CH₂Cl₂, **3**·CH₂Cl₂ and **5**·CH₂Cl₂ crystallize in the monoclinic system with the space group P2(1)/c, while **4**·CH₂Cl₂ crystallizes in the triclinic system with the space group $P\overline{1}$. The crystal data and select refinement details of complexes **1**, **2**·CH₂Cl₂, **3**·CH₂Cl₂, **4**·CH₂Cl₂ and **5**·CH₂Cl₂ are presented in Tables 1 and 2. The ORTEP drawings of the cations and some weak interactions in the crystal structures for **1**, **2**·CH₂Cl₂, **3**·CH₂Cl₂, **4**·CH₂Cl₂ are depicted in Figs. 1–5, respectively.

The X-ray structural analysis shows that all the complexes 1–5 have a mononuclear structure, similar to those reported before [1,7]. The copper(I) ion in each complex adopts a distorted tetrahedral coordinated geometry and is coordinated by two nitrogen atoms from chelating diimine ligands and two phosphorus atoms from the chelating bdpp moiety. The distortion is mainly induced by the N1-Cu1-N2 and P1-Cu1-P2 bite angles which are restricted by the chelating diimine and bdpp ligands. The N1-Cu1-N2 angles are 81.0(1)°, 80.7(2)°, 80.5(2)°, 81.0(2)° and 81.9(2)° for **1**, **2**·CH₂Cl₂, 3 CH₂Cl₂, 4 CH₂Cl₂ and 5 CH₂Cl₂, respectively, whereas the corresponding P1-Cu1-P2 angles are 92.5(1)°, 90.7(1)°, 90.4(1)°, $87.0(1)^{\circ}$ and $91.0(1)^{\circ}$, respectively. The dihedral angles between the planes Cu1-P1-P2 and Cu1-N1-N2 are 79.6°, 91.6°, 92.9°, 92.0° and 89.6°, respectively, in complexes 1-5. The Cu-N and Cu-P bond lengths are in the ranges 2.007(6)-2.092(5) and 2.216(1)–2.281(2) Å, respectively, which are in good agreement with the lengths in analogous systems [1b,1e].

Table 1

Crystallographic data and select refinement details for 1, 2 ·CH₂Cl₂ and 3 ·CH₂Cl₂.

Table 2

Crystallographic data and select refinement details for 4-CH₂Cl₂ and 5-CH₂Cl₂.

	$4 \cdot CH_2Cl_2$	$5 \cdot CH_2Cl_2$
Empirical formula Formula weight T (K) Wavelength (Å) Crystal system Space group	C ₄₃ H ₃₄ Cl ₃ CuN ₂ O ₄ P ₂ 874.55 293(2) 0.71073 triclinic PĪ	C ₄₃ H ₃₂ Br ₂ Cl ₃ CuN ₂ O ₄ P ₂ 1032.36 293(2) 0.71073 monoclinic P2(1)/c
Unit cell dimensions a (Å) b (Å) c (Å) α (°) β (°)	12.497(3) 13.396(3) 15.054(3) 73.95(3) 68.54(3)	12.931(3) 18.021(4) 18.568(4) 101.84(3)
γ (°) <i>V</i> (Å ³) <i>Z</i> <i>D</i> _{calc} (Mg m ⁻³) μ (mm ⁻¹)	63.46(3) 2078.8(7) 2 1.397 0.839	4234.9(15) 4 1.619 2.712
F(000) Reflections collected Independent reflections Reflections with $[l > 2\sigma(l)]$ Data/restraints/parameters Goodness-of-fit (GOF) on F^2 Final R indices $[l > 2\sigma(l)]$ $wR_2 [l > 2\sigma(l)]$ R indices (all data)	896 16298 9422 4928 9422/0/496 0.950 0.0778 0.2153 0.1320	2064 24 050 9626 6948 9626(0/515 1.140 0.0885 0.1833 0.1228
why (dif udid)	0.2000	0.2020

2.2.1. Weak interactions

In the crystal structure of complex **1**, as shown in Fig. 1, one cation links another two on both sides through $C-H\cdots\pi$ interactions between C33–H33A of the pyridine ring at the 4-position and the central phenyl ring of bdpp at the *x*, 0.5 - y, -0.5 + z position ($d_{C33\cdots X1} = 3.596$ Å, C33–H33A···X1 = 144°, and X1 denotes the centroid of the central phenyl ring of bdpp at the *x*, 0.5 - y, -0.5 + z position), leading to a 1-D chain structure along the *c* axis. The 1-D chain structures of the cations are further connected to

	1	$2 \cdot CH_2 Cl_2$	$3 \cdot CH_2Cl_2$
Empirical formula	$C_{40}H_{32}ClCuN_2O_4P_2$	$C_{41}H_{32}Br_2Cl_3CuN_2O_4P_2$	$C_{45}H_{34}Cl_3CuN_2O_4P_2$
Formula weight	765.61	1008.34	898.57
Т (К)	173(2)	293(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2(1)/c	P2(1)/c	P2(1)/c
Unit cell dimensions			
a (Å)	16.426(2)	12.423(3)	12.536(3)
b (Å)	10.893(1)	18.374(4)	18.746(4)
<i>c</i> (Å)	20.777(3)	18.817(4)	18.984(4)
α (°)			
β (°)	103.859(7)	104.98(3)	105.62(3)
γ (°)			
$V(Å^3)$	3609.2(7)	4149.2(14)	4296.4(15)
Ζ	4	4	4
D_{calc} (Mg m ⁻³)	1.409	1.614	1.389
$\mu (\mathrm{mm}^{-1})$	0.812	2.766	0.814
F(000)	1576	2016	1840
Reflections collected	29432	34011	21259
Independent reflections	6342	7287	7531
Reflections with $I > 2\sigma(I)$	4879	6574	3463
Data/restraints/parameters	6342/0/451	7287/0/497	7531/74/570
Goodness-of-fit (GOF) on F^2	1.055	1.144	1.067
Final R indices $[I > 2\sigma(I)]$	0.0537	0.0643	0.0694
$wR_2 [I > 2\sigma(I)]$	0.1205	0.1415	0.1739
R indices (all data)	0.0747	0.0734	0.1705
wR ₂ (all data)	0.1322	0.1467	0.2583



Fig. 1. ORTEP drawing of the chain structure of the cation in the crystal structure of complex **1** along the *c* axis, with the atom labeling scheme, showing 30% thermal ellipsoids. Most hydrogen atoms are omitted for clarity. Selected bond parameters: Cu1-N1 = 2.031(3), Cu1-N2 = 2.015(3), Cu1-P1 = 2.216(1) and Cu1-P2 = 2.237(1)Å; $N1-Cu1-N2 = 81.0(1)^\circ$, $N1-Cu1-P1 = 129.0(1)^\circ$, $N1-Cu1-P2 = 108.7(1)^\circ$, $P1-Cu1-P2 = 92.5(1)^\circ$, $N2-Cu1-P1 = 124.1(7)^\circ$ and $N2-Cu1-P2 = 124.6(1)^\circ$.



Fig. 2. ORTEP drawing of the cation dimer of **2**·CH₂Cl₂ with the atom-labeling scheme, showing 30% thermal ellipsoids. Most hydrogen atoms are omitted for clarity. Selected bond parameters: Cu1–N1 = 2.069(4), Cu1–N2 = 2.011(4), Cu1–P1 = 2.241(2) and Cu1–P2 = 2.241(1) Å; N1–Cu1–N2 = 80.7(2)°, N1–Cu1–P1 = 111.7(1)°, N1–Cu1–P2 = 116.1(1)°, P1–Cu1–P2 = 90.7(1)°, N2–Cu1–P1 = 127.7(1)° and N2–Cu1–P2 = 130.7(1)° (symmetry code for C: -x + 1, -y + 1, -z + 2).



Fig. 3. ORTEP drawing of the cation dimer of **3**-CH₂Cl₂ with the atom-labeling scheme, showing 30% thermal ellipsoids. Most hydrogen atoms are omitted for clarity. Selected bond parameters: Cu1–N1 = 2.074(6), Cu1–N2 = 2.007(6), Cu1–P1 = 2.245(2) and Cu1–P2 = 2.242(2) Å; N1–Cu1–N2 = 80.5(2)°, N1–Cu1–P1 = 117.9(2)°, N1–Cu1–P2 = 110.9(2)°, P1–Cu1–P2 = 90.4(1)°, N2–Cu1–P1 = 130.9(2)° and N2–Cu1–P2 = 127.2(2)°.

each other through C-H \cdots O hydrogen bonds (see Table S1) into a 3-D network.

In the crystal structure of complex $2 \cdot CH_2Cl_2$, a cation dimer is formed through $\pi \cdots \pi$ and double $C-H \cdots \pi$ interactions (see Fig. 2). The former occurs between two exactly parallel pyridine

rings – the ring consisting of C6, C7, C8, C9, C10 and N2 atoms and its symmetric ring at the -x + 1, -y + 1, -z + 2 position (intercentroid distance 3.609 Å, perpendicular distance 3.474 Å, offset 0.981 Å), and the latter occurs between C8–H8A at the 4-position of BrbpyBr and one of the side phenyl rings of bdpp connected to



Fig. 4. ORTEP drawing of the cation dimer of $4 \cdot CH_2Cl_2$ with the atom-labeling scheme, showing 30% thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond parameters: Cu1–N1 = 2.059(4), Cu1–N2 = 2.062(4), Cu1–P1 = 2.260(2) and Cu1–P2 = 2.281(2) Å; N1–Cu1–N2 = 81.0(2)°, N1–Cu1–P1 = 127.9(1)°, N1–Cu1–P2 = 122.7(1)°, P1–Cu1–P2 = 87.0(1)°, N2–Cu1–P1 = 125.6(1)° and N2–Cu1–P2 = 117.1(1)°.

P1 ($d_{C8...X2}$ = 3.682 Å, C8–H8A···X2 = 149°, X2 is the centroid of the phenyl ring of C29C–C34C. C: -x + 1, -y + 1, -z + 2). The cation dimers link each other through another C–H··· π interaction into a 1–D chain structure (see Fig. S1 and Table S2). These 1-D chains are further linked through C–H···O hydrogen bonds ($d_{C...O}$ = 3.279–3.470 Å, C–H···O = 131–178°, see Table S1) into a 3-D framework.

In the crystal structure of complex $3 \cdot CH_2Cl_2$, as shown in Fig. 3, the cation dimer is also formed through $\pi \cdots \pi$ and double C-H··· π interactions, which are very similar to those found for complex $2 \cdot CH_2Cl_2$ (see Tables S2 and S3). Every cation dimer is further linked with another four cation dimers through C-H··· π interactions between one of the side phenyl rings of bdpp connected to P2 and C25-H25A, leading to 2-D network (see Table S2 and Fig. S2). The 2-D networks are further linked through C-H···O hydrogen bonds (see Table S1) into a 3-D framework.

In the crystal structure of complex **4**·CH₂Cl₂, the cation dimer is formed through triple $\pi \cdots \pi$ stacking interactions occurring between two exactly parallel rings – the ring consisting of C4, C5, C6, C7, C11 and C12 and its symmetric ring at the -x+2, -y, -z+1 position (intercentroid distance 3.768 Å, perpendicular distance 3.522 Å, offset 1.338 Å), and between two six-membered rings consisting of N1, C1, C2, C3, C4 and C11, and N2, C7, C8, C9, C10 and C12 at the -x+2, -y, -z+1 position (intercentroid distance 3.682 Å, perpendicular distance 3.423 and 3.464 Å) with a dihedral angle 4.87° (see Fig. 4), and also between the other two corresponding six-membered rings consisting of N2, C7, C8, C9, C10 and C12, and N1, C1, C2, C3, C4 and C11 at the -x+2, -y, -z+1 position. Every cation dimer further links with another four through two C–H $\cdots \pi$ interactions (see Table S2) leading to a 2-D network in the *ab* plane (see Fig. S3).

In the crystal structure of $5 \cdot CH_2Cl_2$, a cation dimer is also formed through a $\pi \cdots \pi$ stacking interaction occurring between two exactly parallel six-membered rings (see Table S3 and Fig. 5). Every cation dimmer is further linked with another six cation dimers through two C-H \cdots interactions leading to a 2-D network in the *bc* plane (see Table S2 and Fig. S4). The anions are connected with cations and the solvent DCM molecules through electrostatic attractions and rich C-H \cdots O intramolecular hydrogen bonds (see Table S1).

In summary, $\pi \cdots \pi$ and $C-H \cdots \pi$ interactions widely exist in the crystal structures of complexes **1–5**. It is interesting to note that all the $\pi \cdots \pi$ stacking interactions occur between diimine ligands,

Fig. 5. ORTEP drawing of the cation dimer of complex **5** with the atom-labeling scheme, showing 30% thermal ellipsoids. The hydrogen atoms are omitted for clarity (symmetry code for A: 2 - x, 1 - y, 1 - z). Selected bond parameters: Cu1–N1 = 2.020(5), Cu1–N2 = 2.092(5), Cu1–P1 = 2.234(2) and Cu1–P2 = 2.239(2) Å; N1–Cu1–N2 = 81.9(2)°, N1–Cu1–P1 = 129.1(2)°, N1–Cu1–P2 = 131.2(1)°, P1–Cu1–P2 = 91.0(1)°, N2–Cu1–P1 = 110.5(1)° and N2–Cu1–P2 = 112.0(2)°.

among which the triple $\pi \cdots \pi$ interaction in the cation dimer of complex **4** is the most striking example.

2.3. Photophysical properties

2.3.1. Infrared spectra

All the complexes **1–5** exhibit typical $v(ClO_4^-)$ modes at about 1090 cm⁻¹ in their IR spectra. Complex **3** also displays a $v(C \equiv C)$ mode at 2112 cm⁻¹ and two v(C-H) bands of $C \equiv C-H$ units at 3238 and 3299 cm⁻¹, respectively, indicating the presence of HC \equiv CbpyC \equiv CH.

2.3.2. Absorption spectra

UV-Vis absorption data of 1-5 in DCM solution at room temperature are summarized in Table 3, while the corresponding electronic absorption spectra are depicted in Fig. S5. All the complexes 1-5 display two distinct absorption regions, a high energy region with wavelengths shorter than ca. 360 nm and a low energy band with wavelengths longer than ca. 360 nm. By comparison with the absorptions of bdpp and the corresponding diimine ligands, along with those of the reported $[Cu(bdpp)_2]^+$ and the [Cu(diimine)(PP)]⁺ analogs [1c,1d,7a,7c,8c,9,10,11b,14], the higher-energy intense bands are assigned to $\pi \rightarrow \pi^*$ ligand-centered transitions of bdpp and the corresponding diimine ligands, while the latter lower-energy, new weak and broad bands, should be assigned to metal-to-ligand charge transfer $d\pi(Cu) \rightarrow \pi^*(diimine)$ (MLCT) transitions. The absorption maximum wavelengths of the MLCT bands, λ_{abs} (MLCT), in complexes **1–5** are 414, 442, 465, 422 and 449 nm, respectively. There is the tendency for $\lambda_{abs}(MLCT)$ to shift to lower energy as the conjugated degree of the diimine ligands becomes larger, which can be observed from complex 1 to complex 3, and from complex 4 to complex 5.

2.3.3. Luminescence

The solid-state emission spectra of complexes 1-5 in the crystalline state were investigated at room temperature upon excitation with λ = 300–350 nm for complexes **1–3** and with λ = 300– 430 nm for complexes **4** and **5** (see Fig. S6), and the spectral data, including emission wavelength, emission lifetimes and the solidstate photoluminescence quantum yields of complexes 4 and 5, are summarized in Table 3. Complexes 1-3 display dual emission bands with λ_{max} = 399 and 539, 425 and 564, and 495 and 603 nm, respectively, while complexes 4 and 5 show single broad emission bands with $\lambda_{max} = 553$ and 570 nm, respectively. As shown in Table 3 and Fig. S6, the emission bands show an obvious red shift in the same series when the conjugated degree of the diimine ligands becomes larger from bpy to HC=CbpyC=CH, and from phen to BrphenBr. The use of single crystals, obtained from repeated recrystallization, for luminescence determination rules out the possibility that the high energy emission comes from a minor contamination of the free ligand, so the higher energy emis-

Table 3					
Photophysical	data	of 1-5	at	298	K.

_	1 5			
	Compound	λ [nm] (CH ₂ Cl ₂)	$\lambda_{em} [nm] (\tau_{em} [\mu s])^a (solid)$	$\Phi_{\rm em}{}^{\rm b}$ (solid)
	1	231, 294, 414	399	
			539 (0.406)	
	2	238, 308, 442	425	
			564 (0.456, 2.436)	
	3	229, 274, 315,	495	
		325, 342, 465	603 (0.211)	
	4	237, 293, 422	553 (2.147, 7.418)	0.1833
	5	237, 300, 449	570 (3.401)	0.0358

^a Solid state emission lifetimes were determined under air.

^b Solid-state quantum yields were determined under air.

sion for complexes **1–3** may arise from intramolecular $\pi \rightarrow \pi^*$ ligand-centered transitions and the low energy bands for 1-5 are assigned to the $d\pi(Cu) \rightarrow \pi^*(diimine)$ (³MLCT) excited state [1d,13,15]. The long lifetimes of the lower energy bands in the microsecond range further support such a triple excited state assignment. The double exponential character of the low energy bands for complexes 2 and 4 indicates they may be mixed with some intermolecular ligand to ligand charge transfer (LLCT) character due to the widely existing $\pi \cdots \pi$ and $C-H \cdots \pi$ interactions. To the best of our knowledge, for [Cu(diimine)(PP)]⁺ complexes, only limited examples, such as [Cu(Mepypm)(DPEphos)]BF4 (Mepypm = 4-methyl-2-(2'-pyridyl) pyrimidine, DPEphos = bis[2-(diphenylphosphino)phenyl]ether) and [Cu(ABPQ)(DPEphos)]BF4 (ABPQ = acenaphtho[1,2-b]bipyrido[2,3-h:3,2-f]quinoxaline), displayed dual emission [1a,16]. The dual emission of [Cu(Mepypm)(DPEphos)]BF₄ was due to its geometric bistability based on inversion of the pyrimidine [1a], and those of [Cu(ABPQ)(DPEphos)]BF₄ in CHCl₃ solution at ca. 470 and 600 nm were also assigned to ${}^{1}(\pi \rightarrow \pi^{*})$ ligand-centered transitions and the ³MLCT excited state, respectively [16]. The lifetimes of the ³MLCT excited state for complexes **1–3** are shorter than those of complexes **4** and **5**, which may be due to the free rotation of the C-C bond between the pyridine rings and the less rigid character of the bpy units.

In order to get quantitative data and explore the factors affecting the luminescence, the emission quantum yields of complexes 4 and 5 in the solid state were measured under air (see Table 3). The solid state emission quantum yield of complex 4 is 0.1833, which is much higher than those of Cu(I) complexes of the bi-phen system under nitrogen [17], and very close to those of the highly emissive [Cu(POP)(dmp)]tfpb (POP = bis[2-(diphenylphosphino)phenyl] ether), tfpb = tetrakis(bis-3,5-trifluoromethylphenylborate) and [Cu(xantphos)(dipp)]tfpb (xantphos = 4,5-bis(diphenylphosphino) -9,9-dimethylxanthene, dipp = 2,9-diisopropyl-1,10-phenanthroline) complexes, 0.19 and 0.22, respectively, under oxygen [18]. Mann and co-workers has reported that the highly emissive [Cu (diimine)(PP)]⁺ complexes [Cu(POP)(dmp)]tfpb, [Cu(xantphos) (dmp)]tfpb, [Cu(xantphos)(dipp)]tfpb and [Cu(xantphos)(dipp)] pftpb (pftpb = tetrakis(pentfluorophenyl)borate) are oxygen sensors [18]. Oxygen can quench their luminescence. The sensing ability correlates with the amount of void space calculated from the crystal structures, but the void space is only a necessary, not a sufficient condition for oxygen sensing in this type of compound [18]. Here the void space in the crystal structure of **4**·CH₂Cl₂ is 3.8%, and no residual solvent accessible void is found for complex 5-CH₂Cl₂ using PLATON/VOID [19,20]. The emission quantum yield of complex 4 under air, 0.1833, is ca. five times of that of complex 5, 0.0358, furthering suggesting the void space is a necessary but not sufficient condition for oxygen sensing. It is suggested that the high solid state emissive quantum yield of complex 4 may be related to the triple $\pi \cdots \pi$ stacking interactions in the cation dimer and rich C–H \cdot π interactions in the crystal structure, since these weak interactions could enhance the phosphorescence emission [1c]. The phosphorescence enhancement accompanies an obvious emission blue shift and a longer excited-state lifetime on going from complex 5 to complex 4.

3. Summary

A series of mixed-ligand copper(I) complexes, [Cu(diimine)(bdpp)]ClO₄, were synthesized and characterized. Their structures and photophysical properties have been studied. In the crystal structures of the complexes, $\pi \cdots \pi$ and C–H $\cdots \pi$ interactions widely exist, and all the $\pi \cdots \pi$ stacking interactions occur between the diimine ligands in the cation dimers. The bpy series of

complexes display dual emissions in the solid state, while the phen series exhibit a single emission. The most significant example of weak intermolecular interactions is observed for complex **4**, which displays triple $\pi \cdots \pi$ interactions between the phen ligands and rich C-H $\cdots \pi$ interactions among the cation dimers. These weak interactions are suggested to be the main reasons for the high emissive quantum yield of 18.33% in the solid state for complex **4**.

4. Experimental

4.1. Materials and reagents

The reagents bpy, phen and bdpp were commercially available and were used without further purification. BrbpyBr, BrphenBr, HC=CbpyC=CH and [Cu(CH₃CN)₄][ClO₄] were prepared by the published methods [21–24]. All solvents were purified and distilled by standard procedures before use, except those for spectroscopic measurements, which were of spectroscopic grade. All other reagents were of analytical grade and were used as received.

4.2. Preparation of the complexes

All reactions were carried out under anhydrous and anaerobic conditions using standard Schlenk techniques under an atmosphere of dry argon at room temperature.

4.2.1. [Cu(bpy)(bdpp)]ClO₄ (1)

 $[Cu(CH_3CN)_4][ClO_4]$ (32.6 mg, 0.100 mmol) was added to a degassed DCM solution (10 mL) of bpy (15.6 mg, 0.100 mmol) and bdpp (45.5 mg, 98%, 0.100 mmol). The color of the solution gradually changed to yellow. The solution was then stirred for 1 day at room temperature. After filtration, layering *n*-hexane onto the DCM solution gave the product as yellow crystals in 71% yield (54.0 mg). *Anal.* Calc. for C₄₀H₃₂ClCuN₂O₄P₂: C, 62.82; H, 4.22; N, 3.67. Found: C, 62.57; H, 3.95; N, 3.69%. HRMS (*m*/*z*): 665.1331 [M-ClO₄⁻]⁺ (calcd. 665.1337). IR (KBr, cm⁻¹): 1095vs (ClO₄⁻).

4.2.2. [Cu(BrbpyBr)(bdpp)]ClO₄·CH₂Cl₂ (**2**·CH₂Cl₂)

This complex was prepared by the same procedure as that of **1** except for the use of BrbpyBr instead of bpy. Layering *n*-hexane onto the DCM solution gave the product as orange-yellow crystals in 78.2% yield (78.5 mg). *Anal.* Calc. for $C_{40}H_{30}Br_2ClCu-N_2O_4P_2$ ·CH₂Cl₂: C, 49.01; H, 3.21; N, 2.79. Found: C, 48.96; H, 3.25; N, 2.73%. HRMS (*m*/*z*): 820.9547 [M-ClO₄⁻]⁺ (calcd. 820.9547). IR (KBr, cm⁻¹): 1094vs (ClO₄⁻).

4.2.3. [*Cu*(*HC*=*CbpyC*=*CH*)(*bdpp*)]*ClO*₄·*CH*₂*Cl*₂. (**3**·*CH*₂*Cl*₂)

[Cu(CH₃CN)₄][ClO₄] (32.6 mg, 0.100 mmol) was added to a 20 mL degassed DCM–acetonitrile (v/v = 1:1) solution of HC=CbpyC=CH (20.4 mg, 0.100 mmol) and bdpp (45.5 mg, 98%, 0.100 mmol). The color of the mixture gradually changed to orange-red. The solution was then stirred for 1 day at room temperature, after which the solvent was removed under reduced pressure and DCM was added. After filtration, layering *n*-hexane onto the filtrate gave the product as orange-red crystals in 54.8% yield (49.1 mg). *Anal.* Calc. for C₄₄H₃₂ClCuN₂O₄P₂·CH₂Cl₂: C, 60.27; H, 3.82; N, 3.13. Found: C, 60.36; H, 3.87; N, 3.27%. HRMS (*m*/*z*): 713.1277 [M−ClO₄]⁺ (calcd. 713.1377). IR (KBr, cm^{−1}): 1091vs [*v*(C=CH)], 3299m [*v*(C=CH)], 3238m [*v*(C=CH)], 2112m [*v*(C=C)].

4.2.4. $[Cu(phen)(bdpp)]ClO_4 \cdot CH_2Cl_2$ (4 · CH_2Cl_2)

This complex was prepared by the same procedure as that of **2** except for the use of phen instead of HC \equiv CbpyC \equiv CH. Layering *n*-hexane onto the DCM solution gave the product as yellow crystals

in 51.9% yield (45.3 mg). *Anal.* Calc. for $C_{42}H_{32}ClCuN_2O_4P_2\cdot CH_2Cl_2$: C, 59.17; H, 3.93; N, 3.21. Found: C, 59.08; H, 3.86; N, 3.22%. HRMS (*m*/*z*): 689.1337 [M-ClO₄]⁺ (calcd. 689.1337). IR (KBr, cm⁻¹): 1094vs (ClO₄⁻).

4.2.5. [Cu(BrphenBr)(bdpp)]ClO₄·CH₂Cl₂ (5·CH₂Cl₂)

This complex was prepared by the same procedure as that of **1** except for the use of BrphenBr instead of bpy. Layering *n*-hexane onto the DCM solution gave the product as orange prismatic crystals in 65.4% yield (67.2 mg). *Anal.* Calc. for $C_{42}H_{30}Br_2ClCu-N_2O_4P_2$ ·CH₂Cl₂: C, 50.20; H, 3.14; N, 2.72. Found: C, 50.27; H, 3.17; N, 2.79%. HRMS (*m*/*z*): 844.962 [M–ClO₄]⁺ (calcd. 844.954). IR (KBr, cm⁻¹): 1094vs (ClO₄⁻).

4.3. Crystal structure determination

Crystals suitable for X-ray diffraction studies for 1, 2 CH₂Cl₂, 3·CH₂Cl₂, 4·CH₂Cl₂ and 5·CH₂Cl₂ were obtained by layering *n*-hexane onto the corresponding DCM solutions in the absence of light. They were measured on RIGAKU SCXmini, Bruker Smart APEX CCD and RIGAKU MERCURY CCD diffractometers, respectively, by the ω scan technique at room temperature with graphite-monochromated MoK α radiation (λ = 0.71073 Å). The CrystalClear software package 2005 [25], Bruker SAINT [26] and the CrystalClear software package 2007 [27] were used for data reduction and empirical absorption corrections, respectively. The structures were solved by the direct method. The heavy atoms were located from the E-map, and the remaining non-hydrogen atoms were found in subsequent Fourier maps. The non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically with isotropic thermal parameters. The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL-97 program package [28].

4.4. Physical measurements

Infrared (IR) spectra were obtained from KBr pellets using a Bruker Optics TENSOR 27 FT-IR spectrophotometer. UV-Vis absorption spectra were recorded on a Purkinje General TU-1901 UV-Vis spectrophotometer. Elemental analyses (C, H, N) were carried out on a Perkin-Elmer model 240C elemental analyzer. HRMS analyses were carried out with a Bruker-micro-TOFQ-MS analyzer using a DCM/methanol mixture as the mobile phase. Steady-state emission spectra were recorded with a Hitachi F4500 fluorescence spectrophotometer. Emission lifetimes were determined on an Edinburgh Analytical Instrument (F900 fluorescence spectrometer) under air and the resulting emission was detected by a thermoelectrically cooled Hamamatsu R3809 photomultiplier tube. The photoluminescence yield in the solid state under air at room temperature is defined as the number of photons emitted for per photon absorbed by the system and was measured under air on an Edinburgh Analytical Instrument FLS920 with an integrating sphere established by Wrighton et al. [29].

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Appendix A. Supplementary data

CCDC 826032, 826033, 826034, 826035 and 826036 contain the supplementary crystallographic data for **1**, **2**·CH₂Cl₂, **3**·CH₂Cl₂, **4**·CH₂Cl₂ and **5**·CH₂Cl₂. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2011.12.040.

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