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Photophysical properties of copper(I) and zinc(II) complexes containing phosphinoquinoline ligands

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ABSTRACT

Several copper(I) and zinc(II) complexes with 8-(diphenylphosphino)quinoline (PPh_2qn) or 8-diphenylphosphinoquinaldine (PPh_2qna) have been prepared. These ligands contain both imine and phosphine moieties, which can act as coordinating groups. X-ray analysis of the Cu(I) complexes reveals that $[Cu(PPh_2qn)_2]PF_6$ (**Cu-1**) and $[Cu(PPh_2qn)_2]PF_6$ (**Cu-2**), coordinated by two PPh_2qn and PPh_2qna ligands respectively, are obtained. In the Zn(II) complexes, a structural study shows that $[ZnCl_2(PPh_2qn)]$ (**Zn-1**), $[ZnBr_2(PPh_2qn)]$ (**Zn-2**) and $[ZnI_2(PPh_2qn)]$ (**Zn-3**) are coordinated by one PPh_2qn ligand and two of the corresponding halogeno ligands (Cl^-, Br^- and I^-). In the solid state **Cu-1** and **Cu-2** show luminescence which is assigned to a ^{3}MLCT transition involving π^* of the quinoline group, as shown in the $[Cu(dmp)(diphosphine)]^+$ complexes; due to the reduced bulkiness of the coordination sphere around the copper atom, no emission is observed in solution. **Zn-1** shows a similar emission band to that of free PPh_2qn at both room temperature and 77 K. It suggests the emission bands should be assigned to a ligand-centered (LC) transition. In the solid state, it is found that the emissive energy of the complexes shift to lower energy and the energy depends on the halogeno ligands in the zinc complexes.

1. Introduction

Much attention has been paid to emissive copper(I) complexes containing polypyridine and/or phenanthroline ligands as candidates for practical components for chemical sensors, display devices and solar-energy conversion schemes [1]. In contrast to the hitherto reported heavy metal complexes, the copper-based system is promising due to the comparative cost advantage. Recently, extensive studies of some mixed-ligand copper(I) complexes involving both imines and phosphines have been reported [2–6]. $[Cu(dmp)(DPEphos)]^+$ (DPEphos = bis[2-(diphenylphosphino)-phenyl]ether) exhibits an unprecedented high quantum yield and a long lifetime in CH_2Cl_2 at room temperature [3,4]. Armaroli et al. and our group have also studied the emissive properties of the mixed-ligand $[Cu(dimine)(diphosphine)]^+$ type complexes coordinated by a diimine ligand such as dmp and several types of diphosphine ligand [5,6]. As other alternatives to heavy metal complexes, several zinc(II) complexes with quinoline groups are potentially promising as luminescent probes and as emissive compounds in electroluminescent devices [7,8].

8-Quinolylphosphine derivatives, which have both imine and phosphine moieties, can act as bidentate ligands. Structural studies of several transition metal complexes with 8-diphenylphosphinoquinoline(PPh_2qn) (Chart 1, left) have been reported [9–11]. Photochemical and photophysical properties of several mixed-ligand ruthenium(II) polypyridine complexes with 8-quinolylphosphines have been investigated [12]. It is expected that copper(I) complexes containing this type of ligand can also behave as good emitters, because the ligands have both diimine and phosphine character. As a similar system, dinuclear copper(I) complexes bridged by 2-(diphenylphosphino)pyridine (PPh_2py) ligands have been reported [13]. However, the dinuclear complexes do not keep a rigid structure in solution due to coordination of donor solvent as well as a PPh_2py exchange process. In contrast, PPh_2qn, which can coordinate to a metal center in a chelate fashion, appears to provide discrete compounds even in solution.

We found that the $[Cu(PPh_2qn)_2]^+$ complex is readily prepared and shows emission in the solid state. In this study, the luminescence of such copper(I) complexes with phosphinoquinoline derivatives has been examined. In addition, treatment of zinc

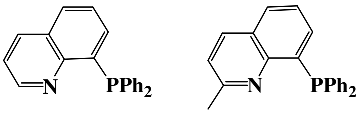

Chart 1. PPh_2qn (left) and PPh_2qna (right).

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halogenide with PPh_2qn readily gave the corresponding $[ZnX_2(PPh_2qn)]$ complexes (X = Cl, Br and I). Zinc complexes coordinated by phosphorus atoms are rare. The luminescence of these complexes are observed in both CH_2Cl_2 solution and in the solid state. In this work, the photophysical properties of the complexes are described in detail.

2. Experimental

2.1. General

8-(Diphenylphosphino)quinoline (PPh_2qn) [14] and $[Cu(CH_3CN)_4]PF_6$ [15] were prepared by the literature methods. 8-(Diphenylphosphino)quinaldine (PPh_2qna) (Chart 1, right) was synthesized by a similar method to that of PPh_2qn, with the use of 8-chloroquinaldine [16]. Each zinc halogenide was purchased from WAKO Chemical Co. Ltd. All reactions were carried under an argon atmosphere using Schlenk techniques until air-stable solid complexes were obtained. Elemental analyses of the complexes were performed on a Perkin Elmer model 2400 CHN analyzer. NMR spectra were obtained using a JEOL Λ-400 spectrometer, in which the chemical shifts are referenced to tetramethylsilane (^1H; as internal) or 85% H_3PO_4 ($^{31}P\{^1H\}$; as external). Absorption and emission spectra were measured with an Agilent 8453 spectrometer and a Shimadzu RF-5000 fluorometer, respectively.

2.2. General procedure to prepare the Cu complexes

PPh_2qn (58 mg, 0.184 mmol) or PPh_2qna (60 mg, 0.183 mmol) was added to a solution of $[Cu(CH_3CN)_4]PF_6$ (34 mg, 0.092 mmol) in $CHCl_3$ (10 ml). The mixture was continuously stirred for 1 h, then the solution was evaporated to a small volume. Addition of diethyl ether to the solution afforded a pale orange precipitate.

$[Cu(PPh_2qn)_2]PF_6$ (Cu-1): Yield: 51 mg (66%). *Anal.* Calc. for $[Cu(C_{21}H_{16}NP)_2]PF_6$ C, 60.40; H, 3.86; N, 3.25. Found: C, 60.22; H, 3.70; N, 3.22%. ^1H NMR ($CDCl_3$) δ 8.49 (d, 1H), 8.18 (d, 2H), 7.96 (d, 1H), 7.79 (t, 1H), 7.31–7.48 (m, 11H). ^{31}P NMR ($CDCl_3$): δ −16.1 (br).

$[Cu(PPh_2qna)_2]PF_6$ (Cu-2): Yield: 48 mg (56%). *Anal.* Calc. for $[Cu(C_{22}H_{18}NP)_2]PF_6$: C, 61.22; H, 4.20; N, 3.25. Found: C, 59.77; H, 4.04; N, 3.07%. ^1H NMR ($CDCl_3$) δ 8.42 (d, 1H), 8.16 (d, 1H), 7.83–7.87 (m, 1H), 7.72 (t, 1H), 7.47 (d, 1H), 7.14–7.20 (m, 10H), 2.0 (s, 3H). ^{31}P NMR ($CDCl_3$): δ −19.2 (br).

2.3. General procedure to prepare the Zn complexes

A solution of $ZnCl_2$, $ZnBr_2$ or ZnI_2 (1.0 mmol) in ethanol (5 ml) was dropped into a solution of PPh_2qn (0.157 g, 0.5 mmol) dissolved in 5 ml $CHCl_3$. The precipitated white powder was filtered and washed with a small amount of ethanol.

$[ZnCl_2(PPh_2qn)]$ (Zn-1): Yield 0.15 g (67%). *Anal.* Calc. for $[ZnCl_2(C_{21}H_{16}NP)]$: C, 56.10; H, 3.59; N, 3.12. Found: C, 55.30; H, 3.34; N, 2.96%. ^1H NMR ($CDCl_3$) δ 9.21 (d, 1H), 8.54 (d, 1H), 8.16 (d, 1H), 7.99 (t, 1H), 7.80 (br, 2H), 7.66–7.70 (m, 4H), 7.47–7.53 (m, 6H). ^{31}P NMR ($CDCl_3$): δ −34.3

$[ZnBr_2(PPh_2qn)]$ (Zn-2): Yield 0.18 g (67%). *Anal.* Calc. for $[ZnBr_2(C_{21}H_{16}NP)]$: C, 46.84; H, 2.99; N, 2.60. Found: C, 55.30; H, 3.34; N, 2.96%. ^1H NMR ($CDCl_3$) δ 9.23 (d, 1H), 8.54 (d, 1H), 8.17 (d, 1H), 7.99 (t, 1H), 7.79–7.83 (m, 2H), 7.66–7.70 (m, 4H), 7.46–7.53 (m, 6H). ^{31}P NMR ($CDCl_3$): δ −36.0.

$[ZnI_2(PPh_2qn)]$ (Zn-3): Yield 0.12 g (38%). *Anal.* Calc. for $[ZnI_2(C_{21}H_{16}NP)]$: C, 39.88; H, 2.55; N, 2.21. Found: C, 55.30; H, 3.34; N, 2.96%. ^1H NMR ($CDCl_3$): δ 9.29 (d, 1H), 8.55 (d, 1H), 8.18 (d, 1H), 7.98 (t, 1H), 7.81–7.84 (m, 2H), 7.65–7.70 (m, 4H), 7.45–7.53 (m, 6H). ^{31}P NMR ($CDCl_3$): δ −37.3.

2.4. X-ray measurements

X-ray crystallographic measurements were made on a Rigaku AFC-5S (for **Cu-1**, **Cu-2** and **Zn-1** at 296 K) or a Rigaku Saturn 70 CCD area detector (for **Zn-2** and **Zn-3** at 123 K) with graphite-monochromated Mo Kα radiation. Absorption corrections were made by the numerical method. Each structure was solved by direct methods (SIR92 [17]) and refined by full matrix least square procedures (SHELXL-97 [18]). The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were fixed at calculated positions. All calculations were carried out by CRYSTAL STRUCTURE software.[1]

3. Results and discussion

3.1. Preparation and characterization of the Cu(I) complexes

Since PPh_2qn has both phosphine-P and imine-N donor atoms, the coordination of two PPh_2qn ligands to the copper(I) ion leads to a similar structure to that of mixed-ligand complexes with diphosphine and diimine ligands. The reaction of $[Cu(CH_3CN)_4]PF_6$ with a two equivalent molar amount of PPh_2qn in $CHCl_3$ readily gave a pale yellow powder of the bis-PPh_2qn copper(I) complex **Cu-1**. The product was identified by elemental analysis and ^1H and $^{31}P\{^1H\}$ NMR spectra. The ^1H NMR spectrum of **Cu-1** shows a symmetric signal set; *e.g.* only one doublet assigned to the proton in the 2-position on a quinoline ring at δ 8.5 appeared The ^{31}P NMR spectrum of **Cu-1** shows a relatively broad signal at δ −16.1, whereas the signal of free PPh_2qn is sharp at δ −17.0. If the signal broadening results from a rapid exchange between the coordination and dissociation of a PPh_2qn ligand in solution, lowering the temperature may cause further broadening based on the splitting of signals assigned to the coordinated and the free ligand. However, the measurement of the ^{31}P NMR spectrum at −40 °C shows a slight sharpening of the signal. So the signal broadening could result from quadrapolar relaxation arising from the copper nucleus, which has been observed for $[Cu(dmpe)]^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane) [19].

Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethylether into an acetone solution of the complex. The molecular structure of $[Cu(PPh_2qn)_2]PF_6$ is illustrated in Fig. 1, and detailed crystallographic data are shown in Table S1. In this complex, the copper atom is coordinated by two bidentate PPh_2qn ligands and has a four-coordinate structure with tetrahedral geometry. Selected bond lengths and angles are summarized in Table 1. The bond lengths of Cu–P are 2.220(1) and 2.229(1) Å. The bite angles for the chelate ring formed by the two PPh_2qn ligands are 87.4(1)° and 86.4(1)°, which are comparable to the other complexes containing PPh_2qn [12b]. The chelate rings are almost planar, as is evident from the torsion angles of Cu–P(1)–C(7)–C(8) (2.4(3)°) and Cu–N(1)–C(8)–C(7) (0.3(5)°). The P–Cu–P bond angle is 131.12(5)°, which is similar to that of $[Cu(dmp)(DPEphos)]BF_4$. One quinoline ring is arranged parallel to the quinoline ring on an adjacent molecule, and the interplanar distance between the quinoline rings is 3.6 Å.

The reaction of PPh_2qna instead of PPh_2qn with $[Cu(CH_3CN)_4]PF_6$ gave **Cu-2**. This product was also identified by elemental analysis and ^1H and $^{31}P\{^1H\}$ NMR spectra. Just as the case of **Cu-1**, a symmetrical signal set for **Cu-2** in the ^1H NMR spectrum was obtained. A methyl singlet of **Cu-2** was observed at δ 2.00, which is shifted to higher field compared to that of free PPh_2qna (δ 2.57)

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[1] CrystalStructure, ver.3.60: Single Crystal Structure Analysis Software, Molecular Structure Corporation.

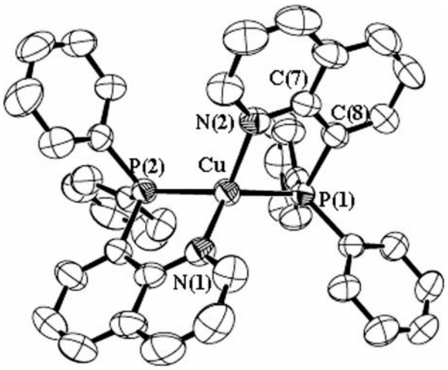

Fig. 1. ORTEP structure of **Cu-1**.

Table 1
Selected bond lengths (Å) and angles (°) for **Cu-1** and **Cu-2**.

Cu-1		**Cu-2**	
Cu–P(1)	2.220 (1)	Cu–P(1)	2.227 (2)
Cu–P(2)	2.229 (1)		
Cu–N(1)	2.071 (4)	Cu–N(1)	2.081 (3)
Cu–N(2)	2.073 (4)		
P(1)–Cu–P(2)	131.12 (5)	P(1)–Cu–P(1)*	118.27 (8)
N(1)–Cu–N(2)	112.1 (1)	N(1)–Cu–N(1)*	112.7 (2)
P(1)–Cu–N(1)	125.4 (1)	P(1)–Cu–N(1)	87.7 (1)
P(2)–Cu–N(2)	116.2 (1)		
P(1)–Cu–N(2)	87.4 (1)	P(1)–Cu–N(1)*	127.5(1)
P(2)–Cu–N(1)	86.4 (1)		

on coordination. The ^{31}P NMR spectrum of **Cu-2** shows a relatively broad signal at δ −19.23.

The crystals of **Cu-2** for X-ray analysis were obtained by slow diffusion of diethylether into a chloroform solution of the complex. The structure of $[Cu(PPh_2qna)_2]PF_6$ is illustrated in Fig. 2. Just as in the case of **Cu-1**, the copper atom coordinated by two PPh_2qna ligands has a four-coordinate structure with a tetrahedral geometry, however the crystal of **Cu-2** has different space group, $C2/c$, compared to $P2_1/c$ for **Cu-1**, as shown in Table 1. A twofold axis goes through the copper atom. Selected bond lengths and angles are summarized in Table 2. The Cu–P and Cu–N bond lengths are 2.227(2) and 2.081(3) Å, respectively, which are similar to those of **Cu-1**. The P–Cu–P bond angle is 118.27(8)°.

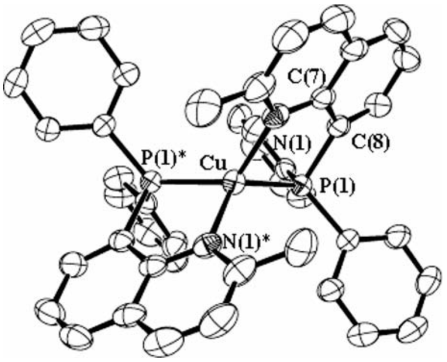

Fig. 2. ORTEP structure of **Cu-2**.

Table 2
Selected bond lengths (Å) and angles (°) for **Zn-1**, **Zn-2** and **Zn-3**.

	Zn-1 (X = Cl)	**Zn-2** (X = Br)	**Zn-3** (X = I)
Zn–X(1)	2.218(2)	2.3601(8)	2.5388(6)
Zn–X(2)	2.201(2)	2.3377(6)	2.5509(6)
Zn–P	2.395(2)	2.395(1)	2.390(1)
Zn–N	2.104(5)	2.096(5)	2.094(3)
X(1)–Zn–X(2)	116.53(6)	115.17(3)	11.9.92(2)
P(1)–Zn–N(1)	82.0(1)	82.4(1)	83.30(9)
P(1)–Zn–X(1)	112.71(6)	113.03(4)	112.53(3)
P(1)–Zn–X(2)	122.95(5)	123.98(4)	117.7(4)
N(1)–Zn–X(1)	106.9(1)	106.8(1)	114.0(1)
N(1)–Zn–X(2)	108.5(1)	108.7(1)	102.6(1)

3.2. Preparation and characterization of the Zn(II) complexes

The treatment of $ZnCl_2$, $ZnBr_2$ and ZnI_2 with PPh_2qn readily afforded **Zn-1**, **Zn-2** and **Zn-3**, respectively. Unlike $[Cu(PPh_2qn)_2]^+$, only one PPh_2qn ligand is coordinated to the zinc(II) ion in these complexes. Attempts to prepare $[Zn(PPh_2qn)_2]$ by treatment of $Zn(PF_6)_2$ without halides failed. Preparation of the $[ZnF_2(PPh_2qn)]$ complex by treatment with ZnF_2 was also unsuccessful. The products were identified by elemental analysis and ^{1}H and ^{31}P{^{1}H} NMR spectra. In the ^{31}P NMR spectra of the complexes, a sharp singlet signal was observed between δ −34 and −39, which shifted to higher field on coordination. Such higher field shifts are hardly ever observed in other Zn(II) complexes containing phosphines [20]. It suggests that the electron density around the phosphorus atom is considerably increased by either the zinc atom or the coordinated halides.

Recrystallization of the zinc complexes did not give single crystals available for X-ray analysis, whereas they were directly obtained by slowly mixing both solutions of PPh_2qn in $CHCl_3$ and ZnX_2 in CH_3OH. The molecular structures of **Zn-1**, **Zn-2** and **Zn-3** are illustrated in Fig. 3. It was found that the PPh_2qn ligand coordinates to the zinc center with two halide ions. Selected bond lengths and angles are summarized in Table 2. and crystallographic data are described in Table S2. The Zn–P bond lengths in these complexes range from 2.390(1) to 2.395(1) Å. Especially, **Zn-3** has the shortest bond length of the reported zinc complexes containing aryl phosphine derivatives [21–23]. The Zn–X bond lengths increase in the order of the following halide ions, Cl, Br and I, however there are no notable differences in the other bond lengths (*e.g.* Zn–N bonds) and bond angles in the three complexes. So the three complexes have a similar coordination environment with regard to PPh_2qn.

3.3. Photophysical properties of the complexes containing phosphinoquinoline ligands

The absorption spectra of **Cu-1** and **Cu-2** in CH_2Cl_2 are shown in Fig. 4. Each complex shows an absorption ranging from 380 to 450 nm, which is not observed for the corresponding free phosphinoquinoline ligand. The Cu–diimine MLCT bands are known to be observed in the region 400–360 nm, with an absorption coefficient of the order of $1.0 \times 10^3\ mol^{-1}\ dm^3\ cm^{-1}$ for mononuclear $Cu-P_2N_2$ complexes [3–6]. It suggests that the absorption bands of **Cu-1** and **Cu-2** are assigned to the MLCT transition from the Cu(I) center to the quinoline moiety. The enhancement of the absorption intensity in the region from 300 to 340 nm for each complex stems from the coordination of the two ligands in one complex molecule. The bands are assigned to the quinoline-based intraligand π–π^* transition, as reported for the ruthenium(II) complexes containing PPh_2qn [12].

Cu-1 and **Cu-2** show emission in the solid state as shown in Fig. 5. The emission maximum of **Cu-1** is located at *ca.* 640 nm. The emission lifetime is estimated at 0.33 μs from the emission decay curve fitted with a single exponential function. The luminescent properties, which are comparable to that of [Cu(dmp)-(diphosphine)]$^+$, suggests that the emission band is assigned to

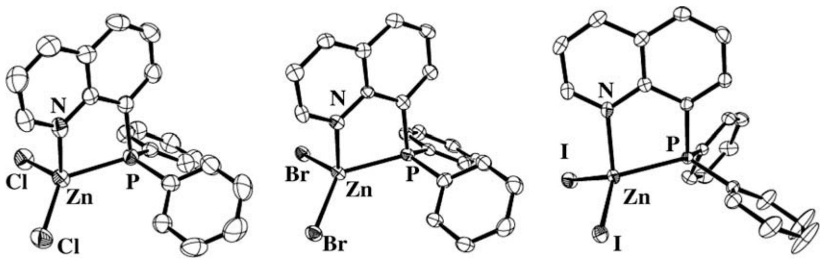

Fig. 3. ORTEP structures of **Zn-1** (left), **Zn-2** (middle) and **Zn-3** (right).

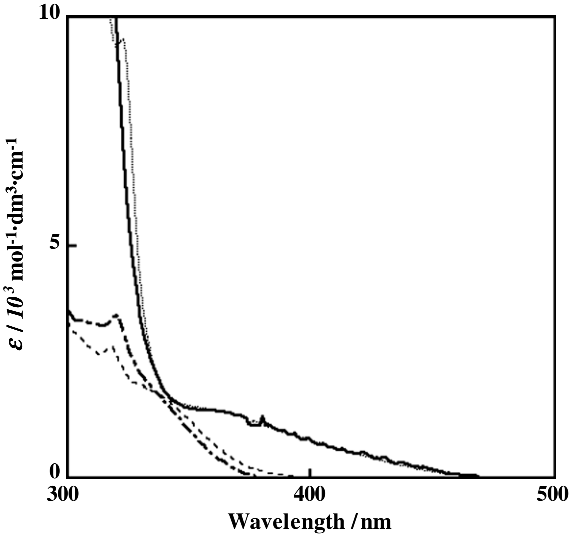

Fig. 4. Absorption spectra of **Cu-1** (solid line), **Cu-2** (dotted line), PPh_2qn (dashed line) and PPh_2qna (dashed-dotted line) in CH_2Cl_2.

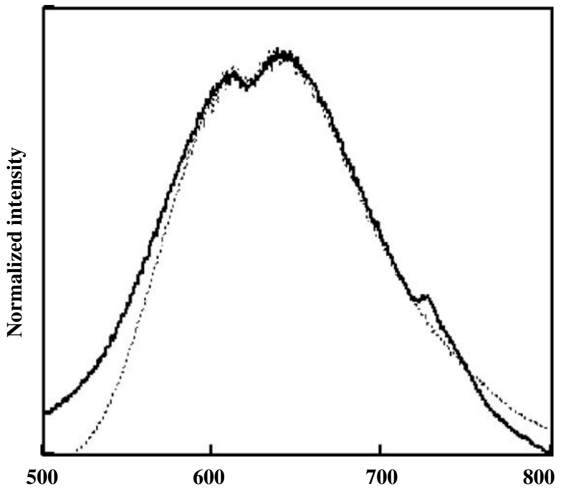

Fig. 5. Emission spectra (uncorrected) of **Cu-1** (solid line) and **Cu-2** (dotted line) in the solid state.

^{3}MLCT transition involving π^* of the quinoline group. The assignment is consistent with the suggestion that no emission is observed in solution because of the lower bulkiness of the coordination sphere around the copper atom in the complex structure, facilitating a tetragonal flattening distortion of the excited luminophore and/or attack of solvent molecules to the excited one in solution. The emission maximum of **Cu-2** is similar to that of **Cu-1**. However, the emission lifetime of **Cu-2** is ca. 1.0 μs, which is three times longer than that of **Cu-1**. In the case of copper(I) complexes containing dmp, it has already been shown that the steric effect of methyl-substituted groups usually results in a higher quantum yield and a longer emission lifetime [2–5]. However, as described in the X-ray structure, the coordination sphere around copper in **Cu-2** is not bulky enough to inhibit quenching of the excited states to emit in solution, even in the presence of the methyl-substituted group in PPh_2qna.

The absorption spectra of the zinc complexes are shown in Fig. 6. All the zinc complexes show similar absorption spectra. Although the free PPh_2qn ligand has an absorption band ranging from 330 to 370 nm, the zinc complexes show smaller intensity in this region. It suggests that the band is assigned to the n–π^* charge transfer transition from the lone pair on the phosphorus atom to the quinoline ring. This type of transition for some metal complexes was reported to have character similar to a protonated aryl phosphine, involving a shift to higher energies compared to the free phosphine [24].

Among the three Zn complexes, only **Zn-1** shows luminescence in CH_2Cl_2 solution at room temperature. As shown in Fig. 7, the emission spectrum of **Zn-1** is similar to that of free PPh_2qn. Therefore, the emission bands are assigned to the ligand-centered (LC) transition. Dissociation of PPh_2qn from **Zn-1** is not suggested because the ^{31}P NMR spectrum of **Zn-1** shows a sharp singlet, as described above. The emission lifetime of **Zn-1** is too short to be measured (<20 ns). It suggests that the emission is fluorescent.

The emission spectra in frozen CH_2Cl_2 at 77 K of **Zn-1** and free PPh_2qn show emission maxima at 535 and 530 nm, respectively (Fig. 7). The spectra were independent of the excitation wave-

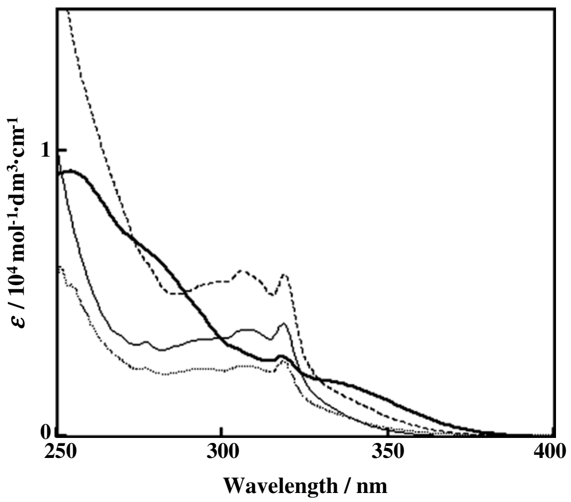

Fig. 6. Absorption spectra of PPh_2qn (bold solid line), **Zn-1** (solid line), **Zn-2** (dotted line) and **Zn-3** (dashed line) in CH_2Cl_2 solution.

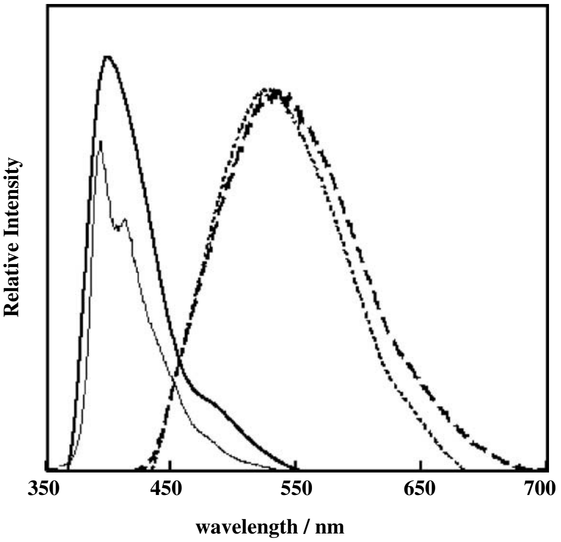

Fig. 7. Emission spectra (uncorrected) of **Zn-1** and PPh_2qn in CH_2Cl_2; **Zn-1** at 298 K (solid line), PPh_2qn at 298 K (bold solid line), **Zn-1** at 77 K (dashed line) and PPh_2qn at 77 K (dotted line).

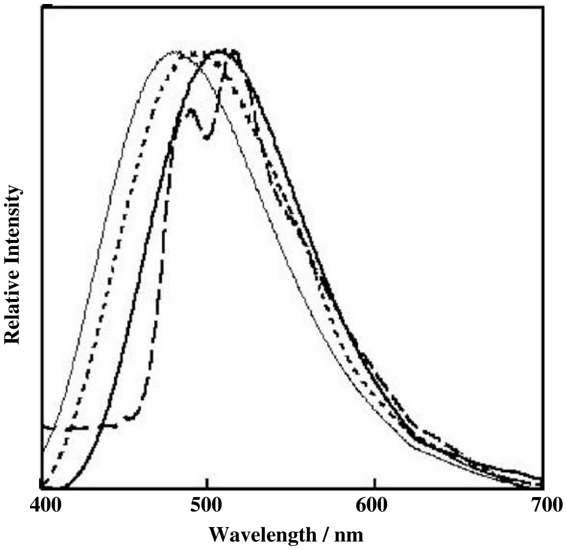

Fig. 8. Emission spectra of PPh_2qn (bold solid line) **Zn-1** (solid line), **Zn-2** (dotted line), **Zn-3** (dashed line) in the solid state at room temperature.

length, over the range 330–350 nm. Fife et al. have reported that the emission spectrum of $[ZnCl_2(PPh_2Me)]$ in diethylether–isopentane–ethanol glass at 77 K show a slightly higher energy emission maximum, at *ca.* 420 nm, than that of free PPh_2Me [24]. The emission band of **Zn-1** is also similar to that of $[Ru(bpy)_2(PPh_2qn)]$ observed in EtOH/MeOH glass at 77 K, which is assigned to a quinoline based $^3(\pi–\pi^*)$ transition [12]. In the case of zinc(II) complexes, a high promotion energy does not result in low-energy MLCT excited states [24]. Thus unlike the Cu(I) complexes, the emission band is assigned to not a metal-to-ligand but to a ligand-centered transition, maybe typically the $(\pi–\pi^*)$ transition in the quinoline ring. One more possibility is a $(n–\pi^*)$-like charge transfer from the Zn–P σ-bond orbital to the π^* orbital on the quinoline ring. However, such a CT emission should be observed at higher energy than that of the corresponding free phosphine [24]. The slight low-energy shift of the emission on coordination to the Zn center suggests that the emission is originates from $\pi–\pi^*$ states.

The emission spectra of the zinc complexes and the free ligand have been obtained in the solid state and are shown in Fig. 8. The emission band of **Zn-1** at *ca.* 500 nm is shifted to lower energy than that in solution, whereas the lifetime is very short (<20 ns). The emission maxima of **Zn-1** and **Zn-2** are slightly shifted to higher energy compared to that of the free PPh_2qn, whereas that of **Zn-3** is observed in the lower energy region and involves vibrational structure; thus the heavier the halogen in the zinc complex, the lower the energy of the emission. The emission energy dependence on the coordinated halogenide ions and structural similarity involving the Zn-PPh_2qn moiety between the complexes suggest that the halogen-to-ligand charge transfer (XLCT) from halogenide to quinoline ring may contribute to the emissive excited states. However, it should be noted that the absorption bands ranging from 300 to 330 nm hardly show any dependence on the halogenide ion, so the character of the excited states associated with the absorption, which may be $\pi–\pi^*$ of the quinoline ring, may differ from that of the emissive excited states.

4. Conclusion

The utilization of PPh_2qn or PPh_2qna, containing both imine and phosphine moieties, successfully gives the new copper complexes **Cu-1** and **Cu-2**, respectively. Both complexes have similar structures to those of mixed-ligand complexes with a P_2N_2 donor set. In the solid state, both Cu(I) complexes show an emission assigned to ^{3}MLCT. However, no emission is observed in solution, even for **Cu-2** coordinated by PPh_2qna which has a bulkier group than PPh_2qn. The bulkiness in the coordination sphere around the copper atom should be smaller than that of the reported mixed-ligand [Cu(dmp)(diphosphine)]-type complexes.

Meanwhile, a series of Zn(II) complexes coordinated by only one PPh_2qn ligand and two halogenide ions was also prepared. All the complexes are stable in solution, and each sharp singlet signal was shifted to amazingly higher field on coordination. Structural characterization shows the similarity of the coordination environment around the PPh_2qn ligand for the three complexes. **Zn-1** shows a similar emission band to that of free PPh_2qn at both room temperature and 77 K. It suggests the emission bands are assigned to a ligand-centered (LC) transition. In the solid state, it is found that the emissive energy of the complex is shifted to lower energy for the series, $Cl^- > Br^- > I^-$. A contribution of the halogenide orbitals in the emissive states is suggested Chart 1.

Appendix A. Supplementary data

CCDC 683537, 683538, 683539, 683540 and 683541 contain the supplementary crystallographic data for **Cu-1**, **Cu-2**, **Zn-1**, **Zn-2** and **Zn-3**. 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. X-ray crystallographic data of the Cu(I) and Zn(II) complexes are shown in Figs. S1 and S2, respectively. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.08.028.

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