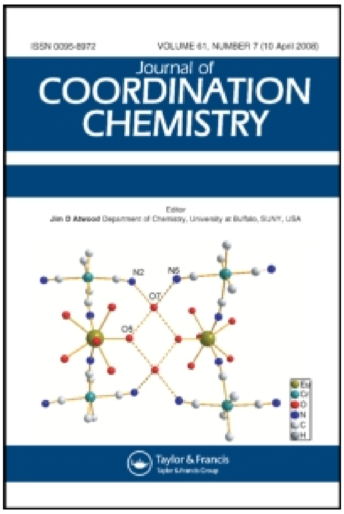

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Syntheses, structures and luminescence of two copper(I)–dppm complexes, dppm = bis(diphenylphosphino) methane

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Two copper(I)–dppm complexes, $[Cu_2(dppm)_2(NMP)_2](ClO_4)_2$ (**1**) (NMP = 2-(4-dimethylaminophenyl)imidazo(4,5-f)(1,10)phenanthroline, dppm = bis(diphenylphosphino) methane) and $[Cu_2(dppm)_2(phen\text{-}NO_2)_2](ClO_4)_2$ (**2**) (phen-NO_2 = 5-nitro-1,10-phenanthroline), were synthesized and their crystal structures were determined by X-ray diffraction. The different ligands chelated to copper(I) give distinct luminescent properties. Complex **1** shows a broad emission ($\lambda_{max} = 523$ nm) in the visible region with short lifetime (0.33 ns), while complex **2** has a large red shift ($\lambda_{max} = 634$ nm) and has longer emission lifetime (0.23 µs) compared with complex **1**. DFT calculations indicate that emission of **1** and **2** originate from singlet ILCT excited states and triplet MLCT excited states, respectively.

Keywords: Copper(I)–dppm; Luminescence; Emission lifetime; DFT calculation

1. Introduction

Photoluminescent properties of d^{10} metal complexes has been receiving attention. A number of polynuclear complexes of Au, Ag, and Cu containing bridging phosphine ligands have been reported which exhibit intriguing photophysical and photochemical properties [1–10]. A key feature in the chemistry of bis(diphenylphosphino)methane (dppm) complexes containing the $Cu_2(dppm)_2$ structural unit is the relative stability of two metal atoms connected by a pair of bridging dppm ligands. Stable $Cu_2(dppm)_2$ framework places much of the burden for structural adjustment on the substrate species themselves and on any additional ligand present [11–16]. In this article, we report the syntheses, structural characterization and luminescent properties of two copper(I) complexes with mixed dppm and L, $[Cu_2(dppm)_2L_2](ClO_4)_2$ (**1**. L = NMP, **2**. L = phen-NO_2). The difference of ligands chelated to copper make the two complexes exhibit distinct luminescent properties in solid state.

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2. Experimental section

2-(4-Dimethylaminophenyl)imidazo(4,5-f)(1, 10)phenanthroline (NMP) [17, 18] and $[Cu_2(dppm)_2(MeCN)_2](ClO_4)_2$ [19] were synthesized by literature procedures. 5-Nitro-1,10-phenanthroline (phen-NO_2) was used as received commercially. Elemental analyses were performed with a Vario EL III CHNOS Elemental Analyzer. Infrared spectra as KBr pellets were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer. The emission spectra were recorded on a FLS920 fluorescence spectrophotometer.

2.1. *Preparation of $[Cu_2(dppm)_2(NMP)_2](ClO_4)_2 \cdot 4H_2O \cdot 2CH_3OH$ (1)*

0.25 mmol of $[Cu_2(dppm)_2(MeCN)_2](ClO_4)_2$ dissolved in 10 mL CH_2Cl_2 and 0.5 mmol NMP dissolved in 10 mL CH_3OH were mixed and stirred at room temperature for half an hour. Orange precipitate was filtrated and washed with CH_3OH (yield 0.36 g, 75%). Orange crystals were obtained by slow diffusion of NMP (CH_3OH solution) into $[Cu_2(dppm)_2(MeCN)_2](ClO_4)_2$ (CH_2Cl_2 solution). Anal. Calcd for $C_{94}H_{94}Cl_2Cu_2N_{10}O_{14}P_4$ (1909.65): C, 59.12; H, 4.96; N, 7.33. Found: C, 59.62; H, 5.02; N, 7.16. IR (solid KBr pellet/cm^{-1}) 1485s, 1434m, 782m, 739s, 715m, 698s, 481m (dppm); 3433s, 1529m, 812m (NMP); 1092vs (ClO_4^{2-}).

2.2. *Preparation of $[Cu_2(dppm)_2(phen\text{-}NO_2)_2](ClO_4)_2 \cdot CH_3CN$ (2)*

0.25 mmol $[Cu_2(dppm)_2(MeCN)_2](ClO_4)_2$ reacted with 0.5 mmol phen-NO_2 in 15 mL CH_3CN at room temperature for half an hour. Yellow crystals were obtained by allowing solvent to evaporate (yield 0.34 g, 86%). Anal. Calcd for $C_{76}H_{61}Cl_2Cu_2N_7O_{12}P_4$ (1586.18): C, 57.55; H, 3.88; N, 6.18. Found: C, 58.02; H, 3.68; N, 6.24. IR (solid KBr pellet/cm^{-1}). 1483m, 1433m, 780m, 739s, 714m, 698s, 479m (dppm); 1514s, 1349s (NO_2); 1092vs (ClO_4^{2-}).

2.3. *X-ray crystallographic analyses*

Suitable single crystal of the two complexes with dimension of $0.47 \times 0.45 \times 0.08\ \mathrm{mm}^3$ for **1** and $0.35 \times 0.30 \times 0.10$ for **2** were carefully selected and glued to thin glass fibers with epoxy resin. Intensity data for the single crystals were collected at 130.15 K on a Rigaku Mercury CCD diffractometer with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using SADABS [20]. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELX97 program package [21, 22]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The crystallographic data are listed in table 1.

2.4. *Calculation details*

DFT calculation on the MO's of $[Cu_2(dppm)_2(NMP)_2]^{2+}$ and $[Cu_2(dppm)_2(phen\text{-}NO_2)_2]^{2+}$ were performed with the Gaussian 03 suite of programs [23] by using method B3LYP and mixed basis sets (Cu CEP-121G; C H 6-31G; N O P 6-31G*).

Table 1. Crystallographic data for **1**, **2**.

Compound	**1**	**2**
Formula	$C_{94}H_{94}Cl_2Cu_2N_{10}O_{14}P_4$	$C_{76}H_{61}Cl_2Cu_2N_7O_{12}P_4$
Formula weight	1909.65	1586.18
Crystal size (mm^3)	0.47 × 0.45 × 0.08	0.35 × 0.30 × 0.10
Crystal color	Orange	Yellow
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pbcn*
a (Å)	17.255(5)	12.958(3)
b (Å)	13.032(4)	22.399(5)
c (Å)	20.222(6)	24.136(6)
β (°)	106.406(4)	
V (Å^3)	4362(2)	7005(3)
Z	2	4
D_{calcd} ($g\,cm^{-3}$)	1.454	1.501
$F(000)$	1984	3244
μ (mm^{-1})	0.697	0.845
θ for data collection (°)	2.10 to 27.48	3.12 to 27.48
Reflections collected	32385	51328
Unique reflections (R(int))	9791 [R(int) = 0.0285]	7944 [R(int) = 0.0391]
Parameters	587	465
GOF	1.082	1.002
R_1, wR_2 ($I > 2\sigma(I)$)	0.0601, 0.1514	0.0670, 0.1916
R_1, wR_2 (all data)	0.0678, 0.1576	0.0723, 0.1964

$R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

The contour plots of MO's were obtained with the GaussianView program. The two models were obtained directly from the crystal structure of complexes **1** and **2**.

3. Results and discussion

3.1. *Syntheses and molecular structures*

Two copper(I) complexes, **1** and **2**, were synthesized by reaction of $[Cu_2(dppm)_2(MeCN)_2](ClO_4)_2$ with NMP and phen-NO_2, respectively. MeCN coordinated to copper(I) is easily replaced by the two 1,10-phenanthroline derivates NMP and phen-NO_2 at room temperature. Perspective views of the cations of **1** and **2** are given in figures 1 and 2. Selected bond lengths and angles are summarized in table 2. Complexes **1** and **2** exist as centrosymmetric dimers. The two dppm molecules bridge two CuL moieties (**1**. L = NMP, **2**. L = phen-NO_2) forming a eight-membered $Cu_2P_4C_2$ metallacyclic ring with ligand NMP or phen-NO_2 chelated to each Cu. There are no Cu···Cu interactions in the cations $[Cu_2(dppm)_2(NMP)_2]^{2+}$ and $[Cu_2(dppm)_2(phen\text{-}NO_2)_2]^{2+}$ with distances of 4.633(2) Å for **1** and 4.595(1) Å for **2**. This is because a conformation occurs in order to avoid close contact between the two coordinated bulks 1,10-phenanthroline derivates, resulting in a large separation of the copper pair. P(1)–Cu–P(2) angles of the two complexes (135.18(3)° for **1** and 136.09(4)° for **2**) are larger than N(1)–Cu–N(2) angles (80.15(9) for **1** and 79.53(12) for **2**), indicating a distorted tetrahedral geometry around the copper atom.

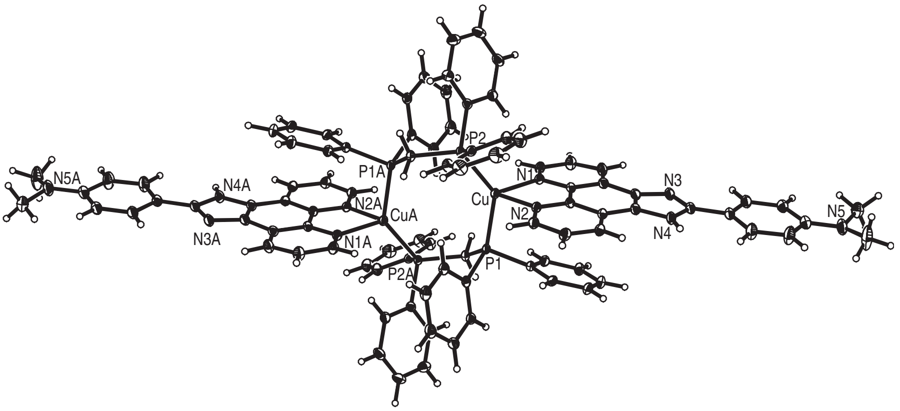

Figure 1. ORTEP drawing of the cation of **1** with 30% probability ellipsoids. Symmetry code: $-x+1, -y, -z$.

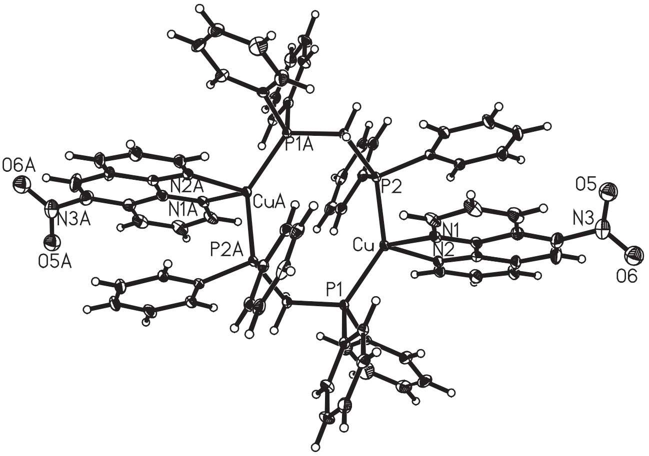

Figure 2. ORTEP drawing of the cation of **2** with 30% probability ellipsoids. Symmetry code: (A) $-x+2, -y, -z+1$, (B) $-x+1, y, -z+3/2$.

Table 2. Selected bond distances (Å) and angles (°).

	1	**2**
Cu–N(1)	2.067(2)	2.087(3)
Cu–N(2)	2.118(2)	2.125(3)
Cu–P(1)	2.2706(8)	2.2207(10)
Cu–P(2)	2.2219(9)	2.2768(10)
N(1)–Cu–N(2)	80.15(9)	79.53(12)
P(1)–Cu–P(2)	135.18(3)	136.09(4)
N(1)–Cu–P(1)	99.57(7)	119.78(9)
N(1)–Cu–P(2)	120.93(7)	100.52(9)
N(2)–Cu–P(1)	97.20(7)	105.54(9)
N(2)–Cu–P(2)	107.26(7)	97.79(9)

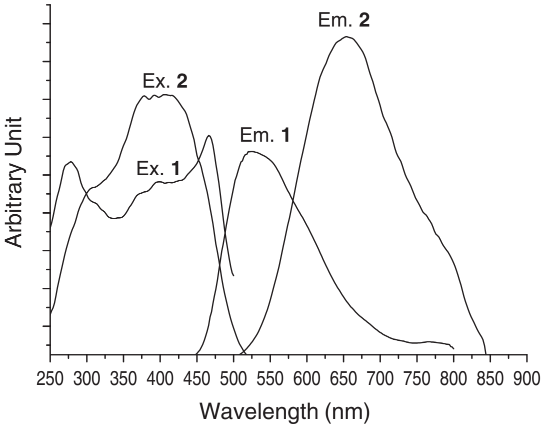

Figure 3. Ambient excitation (left) and emission (right) spectra of **1** and **2** in the solid state.

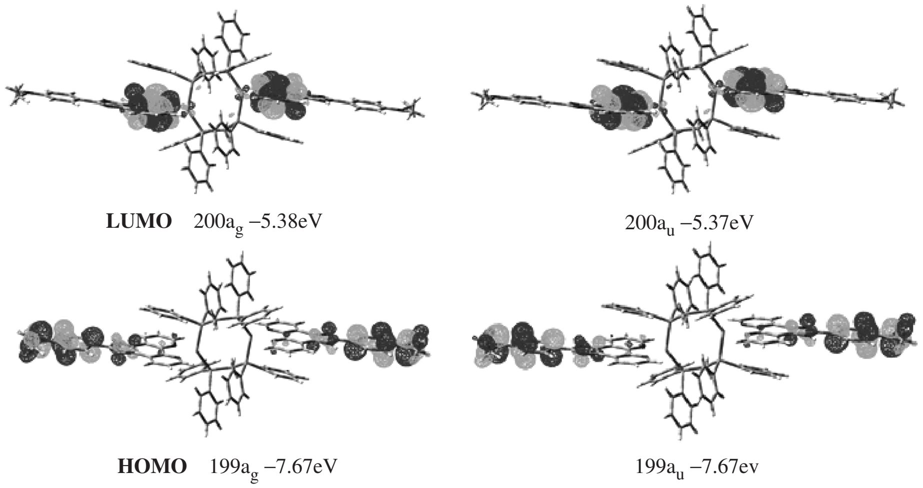

Figure 4. Frontier molecular obitals of $[Cu_2(dppm)_2(NMP)_2]^{2+}$.

3.2. *Luminescence*

Excitation and emission spectra of complexes **1** and **2** in the solid state are shown in figure 3. When excited by 276 nm, complex **1** shows a broad emission in the visible region with a maximum at 525 nm. Several explanations of the emission spectra of copper(I) phosphine complexes, such as phosphine intra-ligand excited state [24], ligand-to-metal charge transfer state [25, 26], metal-cluster-centered excited state [27, 28] or combinations of these have been made. The emission of **1** is neither MLCT (metal-to-ligand charge-transfer) nor LMCT (ligand-to-metal charge-transfer) in nature, and can be assigned to intraligand fluorescent emission, since a very similar emission (with maximum at 522 nm) is observed for free long-conjugated ligand NMP. The conclusion that the luminescene of **1** originates from an ILCT excited state is

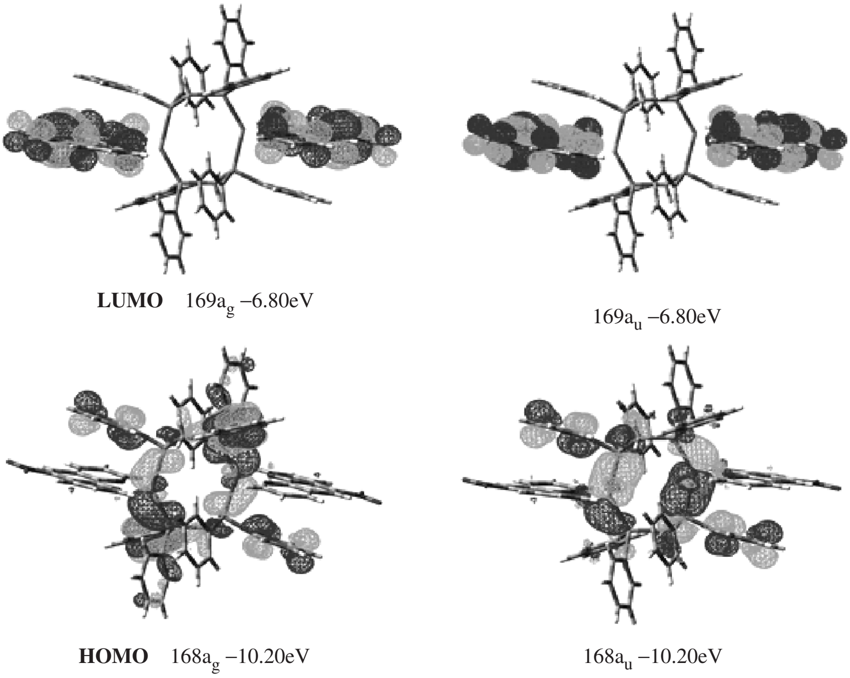

Figure 5. Frontier molecular obitals of $[Cu_2(dppm)_2(phen\text{-}NO_2)_2]^{2+}$.

confirmed by MO calculation on the cation $[Cu_2(dppm)_2(NMP)_2]^{2+}$. As shown in figure 4, the HOMO (199a$_g$ and 199a$_u$) of $[Cu_2(dppm)_2(NMP)_2]^{2+}$ is distributed to dimethylaminophenyl imidazole derivative and the LUMO (200a$_g$ and 200a$_u$) is localized on the phenanthroline derivative. The model $[Cu_2(dppm)_2(NMP)_2]^{2+}$ is too large for excited state calculation, but judging from the plots of frontier orbitals obtained from high-level MO calculations we can guess qualitatively the character of excited state. Very small Stokes shift and short lifetime (0.33 ns) of **1** clearly indicate that emission of **1** is fluorescence. Complex **2** exhibits distinct emission from **1**. When excited at 390 nm, emission of **2** shows a large Stokes shift (with maximum at 654 nm). Emission lifetime (0.23 μs) of **2** is larger than that of **1**. The large Stokes shift and long emission lifetime indicate that emission of **2** is phosphorescence. As shown in figure 5, the HOMO (168a$_g$ and 168a$_u$) of $[Cu_2(dppm)_2(phen\text{-}NO_2)_2]^{2+}$ is mainly metal-localized and the LUMO (169a$_g$ and 169a$_u$) is π^* obitals of phen-NO_2. The emission of **2** arises by the nitryl such that the singlet MLCT excited state of **2** can be easily changed by intersystem crossing into a triplet MLCT excited state from which complex **2** emits.

Supplementary material

CCDC-258205 and CCDC-258204 contain the supplementary crystallographic data for the complexes **1** and **2**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic

Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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