

A New Blue-emitting Diimine Copper(I) Complex: Synthesis, Crystal Structure and Photophysical Properties

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A new diimine Cu(I) complex, [Cu(DPEphos)(DPOP)]BF₄·CH₂Cl₂ (**1**) (DPEphos = bis[2-(diphenylphosphino)phenyl]-ether, DPOP = 2-(11-dipyrido[3,2-a:2',3'-c]phenazine)-5-*p*-tolyl-1,3,4-oxadiazole), has been synthesized and characterized by X-ray single-crystal diffraction analysis. In crystals of complex **1**, the [Cu(DPEphos)(DPOP)]⁺ cations are arranged in supramolecular chains, just like a “zipper”. Cation layers and anion layers are alternating in this structure. The photophysical behavior of DPOP and **1** was studied.

Key words: Cu(I) Complex, Oxadiazole-functionalized Ligand, Photoluminescence

Introduction

The demand for optically functional materials attracts researchers to design functionalized ligands and construct highly sophisticated molecular architectures, incorporating various transition metals, which may have potential applications in solar cells, organic light-emitting diodes (OLEDs), molecular sensors and probes, DNA interactions, supramolecular structures *etc.* [1–5]. One of the earliest and most extensively studied *N*-heterocyclic chelating agents is bidentate 1,10-phenanthroline which is widely employed as a metal-binding component in all aspects of coordination chemistry [6]. The derivatives of 1,10-phenanthroline have also attracted much attention in recent years [2a, 7]. For example, dipyrido[3,2-a:2',3'-c]phenazine (Dppz) was reported in different contexts, foremost in DNA intercalation studies and OLEDs, not only due to its rigid and planar highly conjugated aromatic structure but also its bidentate coordination capacity [8]. Aryl-substituted 1,3,4-oxadiazoles, such as 2-(4-*tert*-butylphenyl)-5-biphenyl-1,3,4-oxadiazole (PBD), are known as efficient electron transporting and hole blocking materials in OLEDs owing to their electron deficiency and good thermal stability [9]. Adachi and co-workers have reported a series of compounds containing the 1,3,4-oxadiazole group and investigated their electroluminescence performances [10]. In

this paper, we designed and synthesized a new ligand and containing the five-membered heterocyclic 1,3,4-oxadiazole group, and studied its photophysical properties. At the same time, we also investigated the effect of metal coordination on absorption and emission properties of the ligand using the Cu(DPEphos) unit. The rich photophysical properties of Cu(I) complexes have attracted a great deal of interest [2a, 11]. Ma and co-workers have fabricated OLEDs based on a tetranuclear Cu(I) complex, however, the reported efficiency was much lower than that of Ir and Pt complexes. Subsequent studies improved the performances of the OLEDs fabricated using Cu(I) complexes by changing the organic ligands [12].

Results and Discussion

Scheme 1 shows the synthetic procedure for the ligand and DPOP. This ligand was reacted with [Cu(MeCN)₄]BF₄ and DPEphos in 1 : 1 : 1 ratio in dichloromethane to give complex **1**.

Description of the structure

Crystal structure analysis has revealed that complex **1** consists of one Cu(DPEphos)(DPOP)⁺ cation, one BF₄[−] anion and one dichloromethane solvent molecule (Fig. 1). In complex **1**, the Cu(I) ion is four-coordinated by two N atoms from DPOP

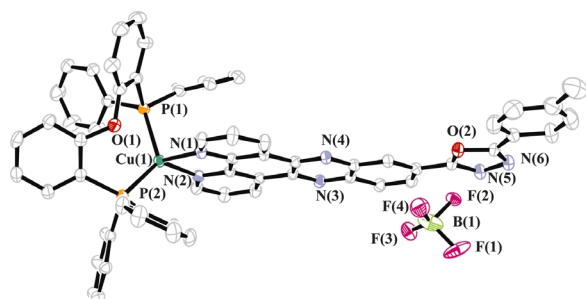
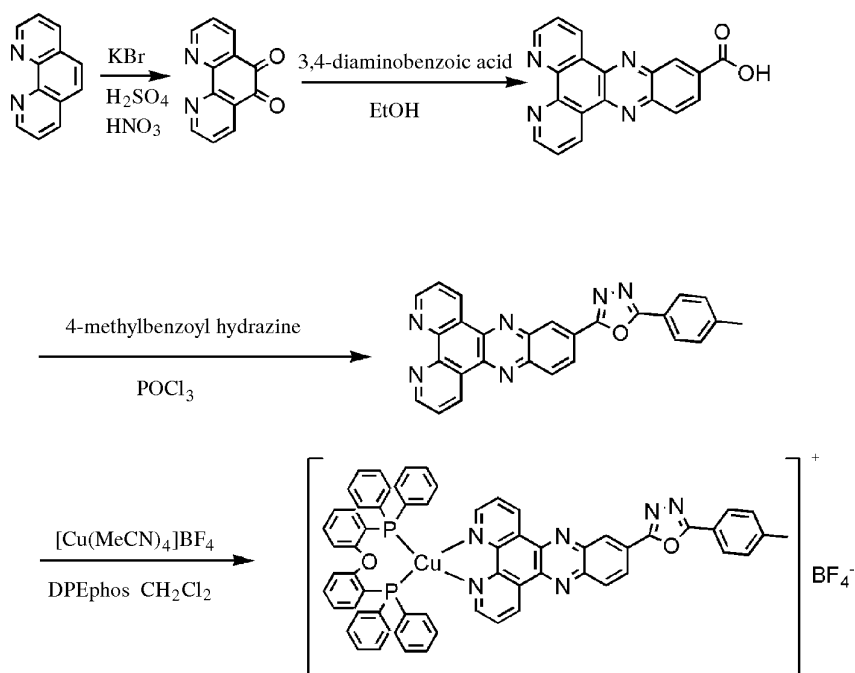


Fig. 1. ORTEP drawing of the molecular structure of **1** in the crystal (hydrogen atoms and the dichloromethane solvent molecule have been omitted for clarity).

and two P atoms from DPEphos, exhibiting a distorted CuN_2P_2 tetrahedral coordination environment. The bond lengths and angles around the copper ion are 2.062(3) and 2.082(3) Å for Cu–N, 2.212(10) and 2.243(11) Å for Cu–P, $81.04(12)^\circ$ for N–Cu–N and $121.06(4)^\circ$ for P–Cu–P, comparable to the parent compounds $[\text{Cu}(\text{dmp})(\text{POP})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$, $[\text{Cu}(\text{phen})(\text{POP})]\text{BF}_4 \cdot 1.5\text{Et}_2\text{O} \cdot \text{CH}_3\text{CN}$ and $[\text{Cu}(\text{dbp})(\text{POP})]\text{BF}_4 \cdot \text{CH}_3\text{CN}$ [2a] and to those in similar four-coordinated Cu(I) complexes [13].

Three parent compounds in ref. [2a] are all based on the phenanthroline ligand and its derivatives dmp and dbp modified by alkyl substituents. Herein, in complex **1**, the organic molecule DPOP with a 1,3,4-

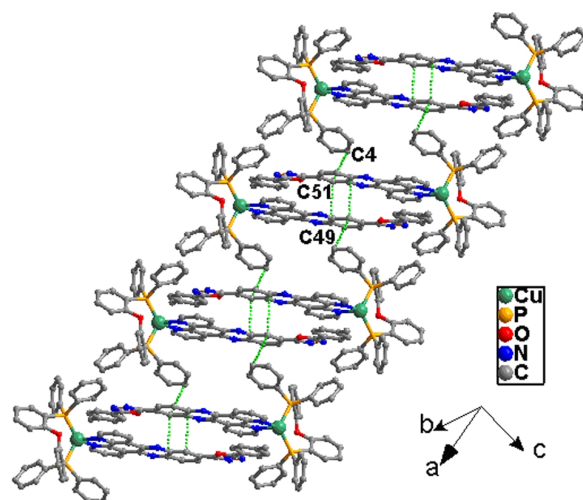


Fig. 2. The aryl packing interactions (broken lines) in crystals of **1** result in a 1D supramolecular “zipper”-like chain.

oxadiazole group has a planar structure, which has an extended conjugated π electron system. In the crystal, the DPOP ligands show strongly offset face-to-face $\pi \cdots \pi$ interactions between neighboring molecules, such as C(51) \cdots C(49): 3.385 Å. Furthermore, the DPOP ligands have $\pi \cdots \pi$ interactions with DPEphos, such as C(4) \cdots C(51): 3.316 Å. These aryl packing interactions result in a 1D supramolecular chain. In-

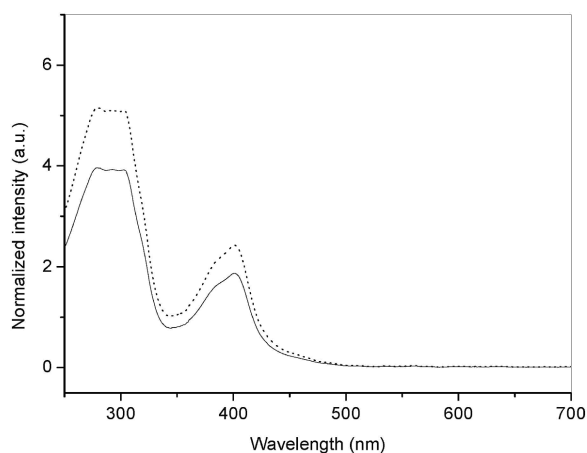


Fig. 3. Normalized UV/Vis absorption spectra of complex **1** (···) and DPOP (—) in CH_2Cl_2 at r. t.

terestingly, in the chain, the $\text{Cu}(\text{DPEphos})(\text{DPOP})^+$ cations are organized like a “zipper” (Fig. 2). These chains are further connected with each other through parallel offset face-to-face $\pi \cdots \pi$ and edge-to-face $\text{C}-\text{H} \cdots \pi$ interactions between the DPEphos molecules, such as $\text{C}(34) \cdots \text{C}(34)$: 3.288 Å, and $\text{C}(20)-\text{H}(20\text{A}) \cdots \text{C}(27)$: 2.841 Å. Therefore, supramolecular cation layers are formed. Along the *a* axis, these cation layers alternate with the layers composed of BF_4^- anions. The aryl packing and electrostatic interactions thus stabilize the structure. By the packing mode of cation and anion layers, micropores are created, which can accommodate the dichloromethane solvent molecules.

Photophysical spectra

Spectroscopic data for DPOP and **1** are presented in Figs. 3 and 4. The ligand Dppz, which is commonly thought to contain partitioned orbital sets, displays limited communication between the phenazine and bipyridyl sections of the ligand [14]. If the ligand DPOP behaves in a similar manner, the introduction of an electron-withdrawing oxadiazole moiety or the coordination to a metal center will show little effect on the properties of the ligand. McMillin and co-workers investigated a series of Cu complexes that had absorption bands in the region 360–400 nm, and the corresponding emission was characteristic of a CT state [2a]. Herein, no changes are found between the ligand and the corresponding complex **1** in the UV/Vis absorption spectra, which means that the

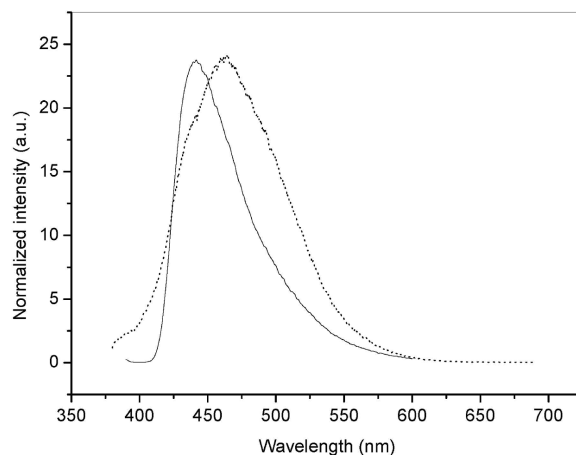


Fig. 4. Normalized emission spectra of complex **1** (···) and DPOP (—) in CH_2Cl_2 at r. t.

metal center contributes very little to the emission of complex **1**. Compared with the emission spectrum of the ligand at 442 nm, that of the complex **1** shows a peak at 462 nm. Both of them emit in the blue region.

Conclusions

In summary, we have designed and synthesized a new ligand DPOP with a 1,3,4-oxadiazole group, and the corresponding Cu(I) complex was prepared and characterized. We also studied the photophysical behavior of DPOP and this Cu(I) complex. In crystals of the title complex, the $\text{Cu}(\text{DPEphos})(\text{DPOP})^+$ cations form a supramolecular “zipper”-like chain through aryl packing interactions. We are currently exploring derivatives of the modular components in order to produce devices with improved properties.

Experimental Section

Materials and methods

All reagents were of reagent grade and were used as received from commercial sources without further purification. ^1H NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer with chemical shifts reported relative to tetramethylsilane. The PL spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. Absorption spectra were measured with a Shimadzu UV-3101PC spectrophotometer. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The IR spectrum was obtained on an Alpha Centaur FT/IR spectrometer with a KBr pellet in the 400–4000 cm^{-1} region. All measurements were carried out in air at r. t.

Table 1. Crystal data and structure refinement for complex **1**.

Formula	C ₆₄ H ₄₆ BCl ₂ CuF ₄ N ₆ O ₂ P ₂
<i>F</i> w	1214.29
Crystal size, mm ³	0.35 × 0.14 × 0.08
<i>T</i> , K	187 (2)
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> , Å	11.9294(9)
<i>b</i> , Å	13.4879(10)
<i>c</i> , Å	22.0434(16)
α , deg	76.9260(10)
β , deg	89.0020(10)
γ , deg	64.8750(10)
<i>V</i> , Å ³	3115.6(4)
<i>Z</i>	2
<i>D</i> _{calcd} , g cm ⁻³	1.294
μ (MoK α), mm ⁻¹	0.547
<i>F</i> (000), e	1244
<i>hkl</i> range	-14 ≤ <i>h</i> ≤ +10; -16 ≤ <i>k</i> ≤ +11; -27 ≤ <i>l</i> ≤ +26
((<i>sin</i> θ)/ λ) _{max} , Å ⁻¹	26.05
Refl. measured/unique	17599/11998
<i>R</i> _{int}	0.0257
Param. refined	759
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)] ^a	0.0656/0.1713
Final <i>R</i> ₁ , <i>wR</i> ₂ (all data) ^a	0.0980/0.1910
GOF (<i>F</i> ²) ^a	0.979
$\Delta\rho_{\text{min}}$ (max/min), e Å ⁻³	1.06/-0.70

^a $R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$, $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}}$, $\text{GoF} = \frac{[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}}{[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}}$.

Synthesis of the ligand DPOP

The 1,3,4-oxadiazole and Dppz units were reacted to form a bifunctional molecule DPOP as outlined in Scheme 1. 1,10-Phenanthroline was treated with H₂SO₄, HNO₃ and KBr to afford 1,10-phenanthroline-5,6-dione [15]. The reaction with equimolar amounts of 3,4-diaminobenzoic acid with HAc as a catalyst in absolute ethanol afforded the Dppz-COOH compound [16]. Dppz-COOH (3.27 g; 10.0 mmol) and 4-methylbenzoyl hydrazine (1.50 g; 10.0 mmol) were dissolved in 30 mL of freshly distilled POCl₃ [17]. The mixture was heated under reflux for 24 h. After excess POCl₃ was removed by distillation under reduced pressure, the mixture was cooled to r. t. and then poured into an ice-water mixture. The precipitate was collected by filtration and washed with sodium hydroxide solution (5 mol L⁻¹) and water. The crude product was collected by Soxhlet extraction in dichloromethane (220 mL) for 6 h. The dichloromethane was removed on the rotary evaporator to give a yellow powder. The yield was 40%. – IR (KBr disc, 25 °C): $\nu = 1031$ (C–O), 1401 (aromatic ring), 1575 (C=N) cm⁻¹. – ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 9.22$ (m, 2H), 8.76 (m, 2H), 8.73 (dd, 1H, *J* = 0.9, 1.8 Hz), 8.50 (dd, 1H, *J* = 2.1, 9 Hz), 8.27 (dd, 1H, *J* = 0.6, 9 Hz), 8.25 (m, 2H), 7.96 (m, 2H), 7.28 (m, 3H), 2.41 (s, 3H).

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

Cu(1)–N(2)	2.062(3)	N(2)–Cu(1)–N(1)	81.04(12)
Cu(1)–N(1)	2.082(3)	N(2)–Cu(1)–P(2)	125.57(9)
Cu(1)–P(2)	2.2122(10)	N(1)–Cu(1)–P(2)	107.10(9)
Cu(1)–P(1)	2.2425(11)	N(2)–Cu(1)–P(1)	108.18(9)
P(1)–C(18)	1.814(4)	N(1)–Cu(1)–P(1)	103.01(9)
P(1)–C(7)	1.816(4)	P(2)–Cu(1)–P(1)	121.06(4)
P(1)–C(1)	1.826(4)	C(18)–P(1)–Cu(1)	113.28(14)
P(2)–C(25)	1.814(4)	C(7)–P(1)–Cu(1)	122.70(13)
P(2)–C(19)	1.825(4)	C(1)–P(1)–Cu(1)	106.98(13)
P(2)–C(31)	1.834(4)	C(25)–P(2)–Cu(1)	118.58(12)
O(1)–C(36)	1.400(5)	C(19)–P(2)–Cu(1)	110.76(12)
O(1)–C(13)	1.401(5)	C(31)–P(2)–Cu(1)	113.39(12)
O(2)–C(56)	1.352(5)	C(37)–N(1)–Cu(1)	129.4(3)
O(2)–C(55)	1.366(5)	C(41)–N(1)–Cu(1)	112.2(2)
C(42)–N(2)–Cu(1)	112.2(2)	C(46)–N(2)–Cu(1)	129.5(3)

Synthesis of [Cu(NCCH₃)₄]BF₄

In a 100 mL round bottom flask were placed 4.0 g of Cu(BF₄)₂·6H₂O, 2 g copper powder and 50 mL CH₃CN. The reaction mixture was heated to 85 °C for 6 h, then the copper powder was removed by filtering the hot solution, and CH₃CN was removed by distillation under reduced pressure. A white solid was obtained [18].

Synthesis of complex **1**

In a 25 mL round bottom flask were placed 538.6 mg (1.0 mmol) DPEphos, 314.0 mg (1.0 mmol) [Cu(CH₃CN)₄]BF₄ and 10 mL CH₂Cl₂. The mixture was stirred for 30 min at r. t. Then 440.0 mg (1.0 mmol) of DPOP was added and the mixture stirred for an additional h and filtered. The clear yellow filtrate was concentrated to 5 mL. CH₃CN (about 5 mL) was added, and vapor diffusion of diethyl ether into the resulting solution gave yellow crystals of the complex [2a]. The yield was 63 % and was dependent on recrystallization losses. Yellowish single crystals of **1** suitable for X-ray diffraction studies were grown by slow evaporation of a dichloromethane solution. – Anal. for C₆₃H₄₄BCuF₄N₆O₂P₂: calcd. C 67.00, H 3.93, N 7.44; found C 66.65, H 3.70, N 7.68. – IR (KBr disc, 25 °C): $\nu = 1030$ (C–O), 1405 (aromatic ring), 1570 (C=N) cm⁻¹. – ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 9.72$ (m, 2H), 9.10 (m, 1H), 8.96 (m, 2H), 8.73 (d, 1H, *J* = 8.1 Hz), 8.54 (d, 1H, *J* = 9.3 Hz), 8.10 (m, 2H), 7.33–6.87 (m, 30H), 2.46 (s, 3H). Further NMR spectra could not be obtained due to solubility problems.

X-Ray crystallography

A single crystal of **1** with dimensions 0.28 × 0.22 × 0.08 mm³ was glued on a glass fiber. Data were collected on a CCD diffractometer with graphite-monochromatized

MoK α radiation ($\lambda = 0.71703 \text{ \AA}$) at 187 K. The structure was refined by the full-matrix least-squares methods on F^2 using the SHELX crystallographic software package [19]. Anisotropic displacement parameters were used to refine all non-hydrogen atoms. All the hydrogen atoms attached to carbon atoms were generated geometrically. The crystal and structure refinement data for complex **1** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

CCDC 704609 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif.

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