

# Synthesis, structure, spectroscopic properties, DFT and TDDFT investigations of copper(II) complex with 2-(2-hydroxyphenyl)benzimidazole

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## Abstract

A Cu(II) complex with 2-(2-hydroxyphenyl)benzimidazole [Cu(pbm)<sub>2</sub>] (**1**), (Hpbm = 2-(2-hydroxyphenyl)benzimidazole) has been prepared and isolated under hydrothermal condition, and its structural and spectroscopic properties thoroughly investigated. The square-planar geometry was verified by both the density functional theory level (DFT) calculation and X-ray crystallography. A further theoretical analysis of electronic structure of this complex has also been undertaken to gain a deeper insight into the properties of relevant molecular orbitals. The time-dependent density functional theory level (TDDFT) calculation, together with DFT-based molecular orbital analyses, demonstrates that the low-lying absorption bands in UV–vis spectrum are all mainly  $\pi \rightarrow d_{x^2-y^2}$  and/or  $(P,\sigma) \rightarrow d_{x^2-y^2}$  ligand-to-metal charge transfer transition (LMCT) in nature.

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## 1. Introduction

The d<sup>9</sup>- and/or d<sup>10</sup>-copper(I, II) complexes have been widely interesting in recent years owing to their physical, chemical and biological properties, such as light-emitting, magnetic, metalloproteinic and supramolecular-isomerized properties [1–5]. Among them, the d<sup>10</sup>-copper(I) complexes have been excellent in photoluminescence and/or electroluminescence [6–8]; while d<sup>9</sup>-copper(II) complexes have been important for their potential ability in magnetic materials [9,10]; more recently some newly found d<sup>10</sup>-copper(I) complexes have also been proven to be much important in stereochemistry for the preparation of supramolecular architectures for various types of molecular polygons, and helix or zigzag chain polymers [5].

Imidazole and its derivatives are an important class of heterocycle with N-donor atoms, therefore they can be excellent organic ligands to generate various complexes upon ligation to both d<sup>9</sup>- and d<sup>10</sup>-copper centers [5,11–13]. For example, the imidazole d<sup>10</sup>-copper(I) systems have demonstrated capacities for construction of inorganic-organic hybrid supramolecular isomers [5], while the imidazole groups of histidyl residuals of some cupric metalloproteins are usually quite important binding sites when coordinated to other metal ions [14,15], so that have profound effects on functions in biological systems.

2-(2-Hydroxyphenyl)benzimidazole (Hpbm = 2-(2-hydroxyphenyl)benzimidazole) has been considered to be another interesting imidazole-derived ligand with N,O-donor atoms in photoluminescence [16,17]. This compound has been found for decades [18], and some d<sup>10</sup>-metal derivative, e.g. [Zn(pbm)<sub>2</sub>], together with photoluminescent properties and theoretical calculations has been investigated previously

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[17], but its copper derivatives have not been available so far.

As a part of program of systematically investigating copper complexes with Hpbm, in this paper we report the synthesis, structure and characterization of copper(II) complex with Hpbm, namely  $[\text{Cu}(\text{pbm})_2]$  (**1**), together with the DFT and TDDFT calculations and analyses for its geometric structure, electronic structure and spectroscopic property.

## 2. Experimental

All the reagents and solvents employed were commercially available and used as received without further purification. The C, H and N micro-analyses were carried out on an Elementar Vario El elemental analyzer. The FTIR spectra were recorded using a Bruker Vector22 spectrometer in the KBr pellets in the range 4000–400  $\text{cm}^{-1}$ . The UV–vis spectra were recorded on a Varian Cary-100 spectrometer. The ESI-MS was carried out on a high-resolution Finnigan MAT LCQ mass spectrometer.

### 2.1. Preparation of $[\text{Cu}(\text{pbm})_2]$ (**1**)

Hpbm was prepared using similar method with slight modification based on literature [18].

To a solution of copper sulfate tetrahydrate (0.1 mmol, 0.025 g) in 5 mL water were added Hpbm (0.2 mmol, 0.042 g) and potassium hydroxide (0.2 mmol, 0.011 g); after stirred vigorously for half an hour, the mixed solution was transferred into a 23 ml Teflon-lined stainless steel autoclave, sealed and heated inside a furnace to 165 °C for 72 h, then slowly cooled to room temperature at a rate of 5 °C per 1 h. Finally, brown block crystals of **1** were recovered by filtration in approximate 75% yield based on Hpbm. ESI-MS ( $\text{CH}_2\text{Cl}_2$ ):  $m/z = 483$   $[\text{CuL}_2 + \text{H}]^+$ . Calcd. for  $\text{C}_{26}\text{H}_{18}\text{CuN}_4\text{O}_2$ : C, 64.79; H, 3.76; N, 11.62. Found: C, 64.85; H, 3.81; N, 11.54%. FT-IR ( $\text{cm}^{-1}$ ): 3433m, 1812w, 1605m, 1564s, 1473m, 1448m, 1401m, 1316w, 1253w, 1146w, 1092w, 1015w, 877w, 825w, 736w, 653w, 565m, 480m, 422w.

### 2.2. X-ray crystallography

Diffraction intensities for **1** were collected at 293 K on a Bruker Smart Apex CCD diffractometer ( $\text{MoK}_\alpha$ ,  $\lambda = 0.71073$  Å). Absorption corrections were applied by using SADABS [19]. The structures were solved with direct methods and refined with full-matrix least-squares technique using SHELXTL program package [20]. The organic hydrogen atoms were generated in ideal positions. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Experimental details of the X-ray analyses are provided in Table 1. Selected bond lengths and angles are listed in Table 2.

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

Compound	<b>1</b>
Empirical formula	$\text{C}_{26}\text{H}_{18}\text{CuN}_4\text{O}_2$
Formula weight	481.98
Crystal system	Orthorhombic
Crystal size/mm	$0.16 \times 0.14 \times 0.03$
Space group	Pbcn (No. 60)
$a/\text{Å}$	11.0225(12)
$b/\text{Å}$	8.0157(10)
$c/\text{Å}$	22.208(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$V/\text{Å}^3$	1962.1(4)
$Z$	4
$D_x/\text{g cm}^{-3}$	1.632
$\mu/\text{mm}^{-1}$	1.148
$F(000)$	988
$\theta$ range for data collection/ $^\circ$	1.83–27.00
Index ranges	$-13 \leq h \leq 10$ , $-10 \leq k \leq 6$ , $-24 \leq l \leq 28$
Total reflections/unique reflections ( $R_{\text{int}}$ )	7340/2113 (0.0354)
Completeness to $\theta_{\text{max}}$	0.986
Observed data/restraints/parameters	2113/0/151
$R_1$ and $wR_2$ [ $I > 2\sigma(I)$ ]	0.0418 and 0.1018
$R_1$ and $wR_2$ (all data)	0.0655 and 0.1148
$S$ on $F^2$	1.031
Largest difference peak and hole/ $e \text{ Å}^{-3}$	0.422 and $-0.298$

### 2.3. Calculation details

The geometric optimization was performed on a Dell precision 490 computer using experimental geometry as input, employing the Gaussian98 suite of programs [21]. The complex was treated as an open-shell system using spin unrestricted DFT wavefunctions (UB3LYP) [22,23], i.e. the Becke three-parameter exchange functional in combination with the LYP correlation functional of Lee, Yang and Parr with 6-31G\* basis set for C, H, N and O atoms, and effective core potentials basis set LanL2DZ for Cu atoms. No symmetry constrains were applied and only the default convergence criteria were undertaken during optimization.

Based on the optimized geometries, time-dependent density functional level (TDDFT) calculations and molecular orbital calculations were performed at the same B3LYP level and basis set to calculate the vertical electron transition energies. The electron density diagrams of molecular orbitals were obtained with the Molden 3.5 graphics program [24].

## 3. Results and discussion

### 3.1. Synthesis

Though the powder crystalline sample of **1** can be readily prepared in solution by simple mixture of solution of copper sulfate with Hpbm in ethanol with a ratio of the former to

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