Novel bright-blue luminescent complex of Zn(II) with 7-amino-methylchromen-4-one: Synthesis, photophysical properties and DFT calculations

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ABSTRACT

A new Zn(II) complex with 7-amino-2-methylchromen-4-one as monodentate ligand has been synthesized and characterized by elemental analysis, MS-FAB, ^{1}HNMR and FT-IR spectroscopy. The structure and spectroscopic properties of complex were studied using X-ray crystallography, fluorescence spectroscopy and DFT calculations. The relationship between solid-state fluorescence and molecular packing of ligand and complex were examined. Fluorescence properties of the solid-state complex (intensive bright-blue emission) indicate that it can serve as a potential photoactive material. The complex could also act as sensitive fluorescent probe for Zn(II) in acetonitrile.

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1. Introduction

The metal coordination compounds exhibiting fluorescence have received much attention due to their important applications as fluorescent sensor in solution and solid state light emitting diodes [1]. Among transition metals zinc complexes can be used as an effective white light emissive and electron transport material in electroluminescence device [2,3]. On the other hand zinc is physiologically important trace element thus the highly selective and sensitive detection of Zn(II) ions is of great importance [4,5]. A variety of fluorescent Zn(II) ions sensors based on different mechanisms: chelation-enhanced fluorescence (CHEF) [6,7], photoinduced electron transfer (PET) [8] or internal charge transfer (ICT) [9] have been reported. Fluorescent probes for Zn(II) ions in biological systems have extensively been characterized by Jiang and Guo [10]. This review focus on sensor design strategy based on molecular structure and mechanism of fluorescence. Among diverse fluorescent zinc sensors most of them derived from nitrogenous heterocycle compounds, especially quinoline, pyridine, bezimidazole and polyamine. Moreover the fluorescent complexes of Zn(II) with ligands containing nitrogen and oxygen donor atoms exhibit blue emission which is very useful for full-color flat panel display technology [11].

Here we present results of synthesis, structure study and photophysical properties of Zn(II) complex with simple molecule – 7-amino-2-methylchromen-4-one as ligand. The ligand and complex were characterized by ^{1}HNMR, IR and MS spectroscopy and by quantum chemical calculations using density functional theory (DFT). The relationship between solid-state fluorescence and molecular packing of ligand and complex as well as the effect of solvent polarity on their emission and excitation spectra in solution were examined.

2. Materials and methods

7-Amine-2-methylchromen-4-one and zinc chloride ($ZnCl_2$) were purchased from Sigma–Aldrich Chemicals (Germany). All substances were used without further purification. Solvents for synthesis and spectroscopic measurement (acetonitrile, methanol, ethanol, DMSO, hexane) were reagent grade. The melting points were determined using an Electrothermal Buechi540 apparatus and they are uncorrected. The IR spectra were recorded on a Shimadzu FTIR 8400S Spectrophotometer in KBr pellets. The ^{1}H NMR spectra were registered at 300 MHz on a Varian Mercury spectrometer. For the new compound satisfactory elemental analyses (0.4% of the calculated values) were obtained using a Perkin Elmer PE 2400 CHNS analyser.

Absorption spectra were recorded using Shimadzu spectrophotometer in 1 cm quartz cuvette. Fluorescence measurements

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Table 1
Crystal structure data for ligand **1** and complex **2**.

Formula	$C_{10}H_9NO_2$ (**1**)	$C_{22}H_{21}Cl_2N_3O_4Zn$ (**2**)
M_r	175.184	527.69
Crystal size (mm)	$0.32 \times 0.10 \times 0.08$	$0.2 \times 0.15 \times 0.15$
Crystal system	$P2_12_12_1$	$P\bar{1}$
Space group	orthorhombic	triclinic
a (Å)	4.8087(9)	7.9838(5)
b (Å)	8.4817(15)	10.3903(6)
c (Å)	21.019(4)	15.1336(9)
α (°)	90	98.527(5)
β (°)	90	99.536(5)
γ (°)	90	107.386(5)
V (Å³)	857.3(3)	1155.10(12)
Z	4	2
D_{calc} (g cm⁻³)	1.357	1.517
μ(Mo Kα) (cm⁻¹)	0.096	1.328
$F(000)$ (e)		540
T (K)	173(2)	173(2)
hkl Range	$-4 \leqslant h \leqslant +6$, $-10 \leqslant k \leqslant +5$, $-16 \leqslant l \leqslant +26$	$-9 \leqslant h \leqslant +9$, $-12 \leqslant k \leqslant +12$, $-18 \leqslant l \leqslant +18$
Reflections measured	2925	11611
Observed reflections	852	3539
R_{int}	0.0299	0.0400
Flack parameter	−1(2)	–
Reflections in refinement	1042	4522
Parameters	119	308
$R(F)/wR(F^2)^a$ (all reflexions)	0.0541/0.1051	0.0563/0.0810
Weighting scheme[b]	0.0531/0.0125	0.0221/0.0
Hydrogen refinement	constr	mixed
GOF (F^2)[c]	1.066	1.066
$\Delta\rho_{fin}$ (max./min.) (e Å⁻³)	0.160/−0.166	0.361/−0.444
Device type	Oxford XCalibur	Oxford XCalibur
Solution/refinement	SHELXS-97/SHELXL-97 [3,4]	SHELXS-97/SHELXL-97 [3,4]

[a] $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$.
[b] $wR_2 = [\sum [w(F_0^2 - F_c^2)^2]/\sum [w(F_0^2)^2]]^{1/2}$; $w = [\sigma_c^2(F_0^2) + (xP)^2 + yP]^{-1}$ and $P = (F_0^2 + 2F_c^2)/3$.
[c] GOF $= \{\sum [w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ (n = number of reflections; p = total number of parameters).
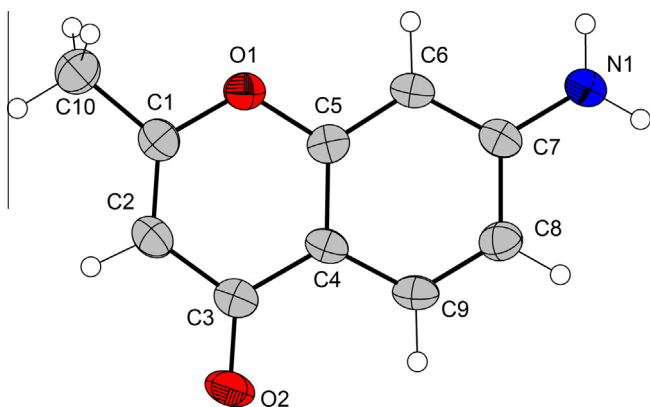

Fig. 1. View of the molecular structure of $C_{10}H_9NO_2$ (1) in the crystal showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

(excitation and emission spectra) in solution were performed on a Shimadzu RF5301 spectrofluorimeter equipped with a 150 W Xenon lamp and 10 mm quartz cells. A powder sample of the subject compound was measured using a quartz plate.

Fluorescence quantum yield (Φ) in solution was determined based on integrating area under the fluorescence curves using quinine sulfate as the standard ($\Phi_f = 0.546$ in 0.5 M H_2SO_4) [12].

Fluorescence lifetimes were determined using time-correlated single photon counting. The samples were excited with a PicoHarp PDL800-D pulsed diode with a centre wavelength of 375 nm. The emission was monitored at 440 nm. IRF was measured at excitation wavelength using a scattering Al slab. The intensity data were

convoluted with the instrument response and evaluated with the software package FluoFitPro (PicoQuant).

Geometry optimized with B3LYP/6-311++G(d,p) approach in vacuum or with B3LYP/6-31+G(d,p) [13–17] approach in PCM (acetonitrile) with linear response. The range-separated functionals have been used: CAMB3LYP (Coulomb-attenuating method applied to B3LYP) functional [18] and LR (long-range correction) applied to the Perdew–Burke–Ernzerhof (PBE) functional [19]. All calculations were done using GAUSSIAN 09 [20].

2.1. Synthesis of bis(7-amino-2-methyl-4H-chromen-4-one)-N5,N′5-dichlorido-zinc(II) (ZnL₂Cl₂) (2)

The solution of $ZnCl_2$ (0.021 g, 0.15 mmol) in acetonitrile (10 ml) was added dropwise to the solution of ligand **1** (0.052 g, 0.03 mmol) in acetonitrile (15 ml). The reaction mixture was stirred at the room temperature for 2 h. After 24 h, precipitated a yellow solid was filtered off, washed with diethyl ether and dried in the air. Yellow crystals suitable for X-ray of complex **2** were obtained by diffusion to diethyl ether from acetonitrile solution. Yield: 56 mg (90.32%), mp: 191.5–192.8 °C. FTIR (KBr cm⁻¹):

Table 2
Selected bond distances (Å) in the crystal structure of **1**.

Bond	Distances (Å)	Bond	Distances (Å)
C3–O2	1.249(3)	C3–C4	1.453(4)
C1–O1	1.366(3)	C4–C9	1.400(3)
C5–O1	1.383(3)	C4–C5	1.407(4)
N1–C7	1.372(3)	C5–C6	1.380(4)
C1–C2	1.345(4)	C6–C7	1.393(3)
C1–C10	1.481(3)	C7–C8	1.420(4)
C2–C3	1.443(4)	C8–C9	1.377(4)