

Synthesis, structure and electroluminescent properties of Schiff-base boron complex with anilido-imine ligand

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ABSTRACT

The Schiff-base ligand boron complex, LBF₂ [L = *ortho*-C₆H₄(NC₆H₃Me₂-2,6)(CH = NC₆H₃Me₂-2,6)], is synthesized and characterized. The crystal structural study reveals that central boron atom is four coordinate and adopts a distorted tetrahedral geometry in LBF₂. The photo/electroluminescent properties of the boron complex have been studied. The electroluminescent devices were fabricated by doping LBF₂ in polymer blends host of poly(vinylcarbazole) (PVK) and 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD) using simple solution spin-coating technique. The single-layer polymer organic light emitter devices exhibited blue-green emission with maximum current efficiency of 1.6 cd/A and maximum luminance of 840 cd/m².

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1. Introduction

Luminescent coordination complexes have been one of the most active research areas due to their potential application in fields of optoelectronic devices and chemical sensors [1–4]. One of the most important considerations in organic light-emitting diodes (OLEDs) is the design and synthesis of high emission efficiency molecules through the modification of ligands and the selection of center metal [5,6]. Recently, organic boron compounds have attracted much attention due to their good luminescent properties, electron-transporting properties and low cost. For example, a large number of boron compounds based on 8-hydroxyquinoline [7], pyridyl-7-azaindole [8], pyridyl-phenol [9], pyridyl-pyrrolide [10] have been investigated in recent years. Particularly, Wang and co-workers have systematically reported the synthesis, structures and photoluminescent (PL) and electroluminescent (EL) properties of boron-containing compounds. Nevertheless, reports on the Schiff-base ligands boron complexes as emission materials in OLEDs are still scarce. We have recently focused our attention on the synthesis of luminescent complexes with chelating anilido-imine Schiff-base ligands [11–13], where the emission color of complexes in solution can be tuned by the

ortho-substituents on the rotatable aryl rings of the ligands. As we know, the compounds containing rotatable aryl rings, such as silole, have high luminescent efficiency in the solid state [14]. As a continuation of our studies on the luminescent boron complexes, herein we report the structure and EL characterizations of a boron complex with larger volume Schiff-base ligand as emitter in polymer OLEDs by simple spin-coating technology from solution.

2. Experimental details

2.1. Material

BF₃ · Et₂O, *n*BuLi, poly(vinylcarbazole) (PVK), 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were purchased from Aldrich and used as received. *Ortho*-C₆H₄(NHC₆H₃Me₂-2,6)(CH = NC₆H₃Me₂-2,6) (L) was synthesized according to the literature [11].

2.2. Characterizations

The infrared spectrum was recorded on a GX Fourier transform infrared spectrometer (Perkin-Elmer company). The nuclear magnetic resonance (NMR) spectra were measured using a Varian Mercury-300 NMR spectrometer. The elemental analysis was performed on a Perkin-Elmer 2400 analyzer. The diffraction data of LBF₂ were collected at 293 K on Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated

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Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized position. All calculations were performed using the SHELXTL [15] crystallographic software packages. CCDC-668572 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/ deposit. UV-vis absorption spectra were recorded on UV-3100 spectrophotometer. Fluorescence measurements were carried out with RF-5301PC.

Indium-tin-oxide (ITO)-coated glass with a sheet resistance of $<50 \Omega \square^{-1}$ was used as substrate. The substrate was pre-patterned by photolithography to give an effective device size of 4 mm^2 . Pre-treatment of ITO includes a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. Active layers were spin-coated from chloroform solutions containing 20 mg/ml of $x\%$ by weight LBF $_2$ in polymer on ITO substrates to give film thickness of 80–100 nm. The hole block layer BCP was deposited by thermo-evaporation. The cathode Ba/Al was deposited (50 nm) by thermo-evaporation and followed by a thick Al capping layer. The electroluminescence and luminance were recorded on a PR650 spectrometer. Current voltage and light intensity measurements were made at room temperature and ambient conditions.

2.3. Synthesis of LBF $_2$

*n*BuLi (0.52 mmol) was added dropwise via syringe over 10 min to a stirred solution of *ortho*-C $_6$ H $_4$ (NHC $_6$ H $_3$ Me $_2$ -2,6)(CH = NC $_6$ H $_3$ Me $_2$ -2,6) (0.17 g, 0.52 mmol) in 15 ml of toluene at -78°C . The mixture was stirred at -78°C for additional 10 min and allowed to be warmed to the room temperature. After 4 h at room temperature, the resulting mixture was added dropwise to a toluene solution of BF $_3 \cdot \text{Et}_2\text{O}$ (0.64 ml, 0.52 mmol) at -78°C with stirring. The mixture was allowed to warm to the room temperature and was stirred overnight. The mixture was filtered and the filtrate was reduced to approximately 5 ml in volume and kept at -10°C overnight to let the product crystallize. The product was obtained as yellow-green crystals (0.18 g, 78%). Anal. Calcd for C $_{23}$ H $_{23}$ N $_2$ BF $_2$ (376.25): C 73.42, H 6.16, N 7.45. Found: C 73.56, H 6.31, N 7.59. ^1H NMR (CDCl $_3$, 293 K): δ 2.33 (s, 6H, CH $_3$), 2.45 (s, 6H, CH $_3$), 6.35 (d, 1H, Ph-H), 6.80 (t, 1H, Ph-H), 7.28–7.43 (m, 7H, Ph-H), 7.47 (t, 1H, Ph-H), 8.22 (s, 1H, CH = NAr) ppm. ^{13}C { ^1H } NMR (CDCl $_3$, 293 K): δ 18.4 (CH $_3$), 112.0, 114.6, 116.0, 126.9, 128.0, 128.6, 128.7, 133.1, 134.2, 137.3, 138.1, 138.3, 141.9, 151.6, 163.8 (CH = NAr) ppm. IR (KBr, cm $^{-1}$) ν 2924m, 2854w, 1623s, 1554s, 1480m, 1455s, 1382m, 1344s, 1231w, 1190s, 1058s, 1095w, 949w, 763s, 623w, 548w, 521w, 467w.

3. Results and discussions

3.1. Complex synthesis

The boron difluoride complex LBF $_2$ was synthesized in good yields (78%) by the reaction of BF $_3 \cdot \text{OEt}_2$ with the lithium salt of its ligand that was generated in situ by treating the free ligand with *n*BuLi in toluene at -78°C . The complex LBF $_2$ was characterized by elemental analyses, ^1H and ^{13}C NMR spectroscopy, IR-spectroscopy, and satisfactory analytic results were obtained on the complex. In the ^1H NMR spectrum of LBF $_2$, the resonance for the imino CH proton is at $\delta = 8.21$ ppm. While the resonance ($\delta = 163.8$ ppm) for the imino C-atom in the ^{13}C NMR spectrum shifts to higher field in comparison with the corresponding signals of the free ligand and the dichloride aluminum complex [13].

The LBF $_2$ was very soluble in dichloromethane, diethyl ether, toluene and THF, and moderately soluble in saturated hydrocarbons.

3.2. Crystal structure

The molecular structure of the complex LBF $_2$ was determined by X-ray crystallographic analysis. Crystals of the LBF $_2$ suitable for X-ray crystal structure determination were grown from *n*-hexane at room temperature. The ORTEP drawing of molecular structure of LBF $_2$ is shown in Fig. 1. Cell parameters and refinement details for LBF $_2$ are listed in Table 1. In LBF $_2$, the boron center adopts a distorted tetrahedral geometry. The boron center atom is bidentate chelated by the Schiff-base ligand via two nitrogen atoms, and the other two coordination sites are taken up by two fluoride ligands. The N–B–N bite angle in LBF $_2$ ($107.9(2)^\circ$) is larger than this in the aluminum complex with same ligand ($93.86(6)^\circ$) [12], which is presumably due to the smaller atom radii of boron. In the complex, the six-membered chelating ring is nearly planar with the boron atom lying 0.1292 \AA out of the plane. The imino C=N bond in this complex retains its double bond character, being $1.297(2) \text{ \AA}$. The average B–F bond lengths of $1.377(4) \text{ \AA}$ in the boron complex is slightly smaller than $1.403(2) \text{ \AA}$ for 2,2-difluoro-1,3,4,6-tetramethyl-3-aza-1-azonia-2-bora-4,6-cyclohexadiene [16]. The F–B–F bond angle of the complex is $108.5(3)^\circ$, which is close to $107.8(2)^\circ$ for previously reported *p*-Tol $_2$ nacnacBF $_2$ [17]. The dihedral angle between the six-membered chelating ring and the aromatic ring at the amido nitrogen is 84.0° , while the dihedral angle between the six-membered chelating ring and the aromatic ring at the imine nitrogen is 76.3° .

3.3. Photoluminescent and electroluminescent properties

Fig. 2 shows the chemical structures of LBF $_2$, BCP and polymer hosts used in this study. The UV-vis absorption and fluorescence spectra of LBF $_2$ are shown in Fig. 3. The absorption and emission peaks of LBF $_2$ in chloroform are at 425 and 493 nm, respectively. However, LBF $_2$ in the solid state emits bright fluorescence with emission maximum of 508 nm, which is red-shifted in comparison with its emission maximum in solution. The red shift of the emission wavelength from solution to solid state is likely caused by π - π stacking of aromatic rings in the molecule in the solid state. The quantum yield of LBF $_2$ has been determined in chloroform [18], and the high PL efficiency (0.51) should also be

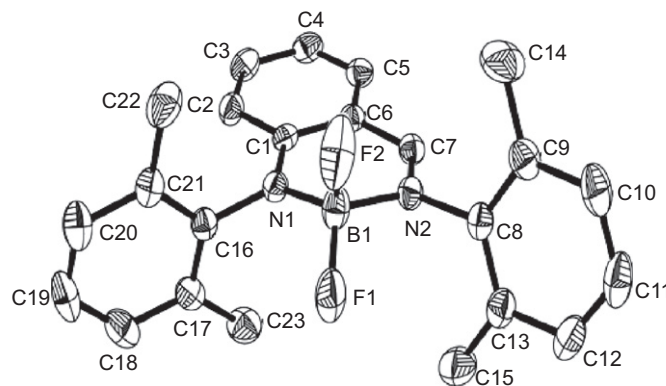


Fig. 1. Molecular structure of LBF $_2$ (thermal ellipsoids are drawn at the 30% probability level). Selected bond lengths (\AA) and bond angles (deg.): B(1)–N(1), 1.519(4); B(1)–N(2), 1.578(4); B(1)–F(1), 1.376(4); B(1)–F(2), 1.378(4); C(1)–N(1), 1.362(3); C(7)–N(2), 1.297(3); F(1)–B(1)–F(2), 108.5(3); N(1)–B(1)–N(2), 107.9(2); F(1)–B(1)–N(1), 110.4(3); F(2)–B(1)–N(1), 113.3(3); F(1)–B(1)–N(2), 110.1(2); F(2)–B(1)–N(2), 106.5(3).

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