



Synthesis of a new boron complex with imine ligand: Synthesis, characterization and fluorescent properties

Pınar Şen*

Uskudar University, Faculty of Engineering and Natural Sciences, Department of Forensic Science, 34662, Istanbul, Turkey; ORCID ID orcid.org/0000-0002-3181-9890

ARTICLE INFO

Article history:

Received 19 June 2018
Revised form 26 January 2019
Accepted 01 February 2019
Available online 16 March 2019

Research Article

DOI: [10.30728/boron.434776](https://doi.org/10.30728/boron.434776)

Keywords:

Fluorine boron complex,
Fluorescence property,
Schiff base ligand,
Synthesis,
Red-shift emission,
Stokes' shift, quantum yield

ABSTRACT

In this study, it is aimed to obtain of N,N'-Bis(3-tert-Butyl-5-methylsalicylidene)-1,2-diaminoethane-boron complex (**3**) in three-step reaction. In the first step, an aromatic aldehyde derivative was synthesized by the o-formylation reaction with commercially available an aromatic phenol. The condensation reaction was carried out to give the imine derivative as a Schiff base ligand (**2**). The fluorine chelated boron complex was synthesized through the reaction of $\text{BF}_3 \cdot \text{OEt}_2$ with ligand (**2**). This Schiff base-boron complex was reported for the first time and was fully characterized by common spectroscopic techniques such as $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FT-IR, UV-Vis, MS and elemental analysis. The spectroscopic properties of the target boron-complex were examined with the absorption and fluorescence spectroscopy. It was determined that the obtained boron complex is highly emissive molecule in different solvents with large Stokes shifts reaching 100 nm. Moreover, the measurements of the fluorescence quantum yields (up to 48%) were performed.

1. Introduction

Fluorescence coordination compounds have drawn considerable attention in the past few years. Boron-dipyrromethene (BODIPY) derivatives, which are BF_2 complex of dipyrromethene unit have been classified organoboron compounds and are one of the most studied types of fluorescent dyes as organic fluorine boron complexes. They have excellent optical properties displaying high emission, high absorption coefficients, and photo-stability [1,2].

These features make it utilizable for many fields such as organic light-emitting diodes [3], fluorescence imaging and labeling [4,5], photosensitizer for photodynamic therapy [6], and fluorescence sensors for the detection of chemically important species [7]. In addition these applications, the research on new fluorine boron complexes have been in progress for boron neutron capture therapy [8] and solar cells [9].

Beside dipyrromethene derivatives, pyrrole-imine [10], bispyrrole [11], pyridyl-phenol [12] and Schiff base ligands [13] have been studied to form four-coordinated boron complexes because of showing good luminescent properties in recent years. Among these chelating agents, boron complexes of Schiff-base ligands have been reported in only a few studies so far.

Schiff base derivatives are one of the most studied li-

gands since this type of ligands could generate stable complexes with most transitions metals as a N₂-O₂ or two N-O chelation.

Thus, in this study, Salen-type Schiff base ligand (**L**, N,N'-Bis(3-tert-Butyl-5-methylsalicylidene)-1,2-diaminoethane (**2**)) was obtained by the condensation of an aromatic aldehyde derivative and ethylenediamine, and the synthesis and characterization of its boron complex (BF_2)₂**L** (**3**) were performed.

The optical and fluorescence properties of the prepared bi-metallic boron complex (**3**) were evaluated by taking measurements in different solvents to observe the effect of polarity.

2. Materials and methods

2.1. Chemicals and instruments

2-tertbutyl-4-methylphenol, urotropin, glacial acetic acid, ethylenediamine, dichloromethane (DCM), chloroform (CHCl_3), methanol (MeOH), toluene, triethylamine (TEA), Boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$), NaHCO_3 were obtained from Sigma-Aldrich. All solvents were dried and purified as reported by Perrin and Armarego [14] before using. Dual-bank vacuum-gas manifold system was used to provide oxygen-free inert atmosphere. The progress of the reactions and chemical purity of the compounds were controlled by

*Corresponding author: pinar.sen@uskudar.edu.tr

TLC using silica gel 60-HF254 as an adsorbent. Silica gel (Merck grade 60) was used at column chromatography to provide purity. Infrared spectra were acquired on a PerkinElmer UATR-TWO diamond attenuated total reflectance (ATR) spectrophotometer. Electronic spectra were obtained on a Hitachi U-2900 UV-Vis spectrophotometer. Fluorescence spectra were recorded from Hitachi F-2710 Fluorescence spectrofluorometer with quartz cell of 1 cm. at room temperature. Acquisition of ^1H and ^{13}C NMR spectra were carried out a Varian Mercury Plus 300 MHz spectrometer. Mass analysis was performed on an Agilent 6230 A LC-TOF/MS Spectrometer. The elemental composition of the target compound was determined by Flash 2000, Thermo Scientific as an element analyzer.

2.2. Synthesis

The synthesis of 3-tert-Butyl-2-hydroxy-5-methylbenzaldehyde (**1**) [15] and N,N'-Bis(3-tert-Butyl-5-methylsalicylidene)-1,2-diaminoethane (**2**) [16] were accomplished according to the reported work. The spectroscopic observations are consistent with the literatures.

2.2.1. Synthesis of N,N'-Bis(3-tert-Butyl-5-methylsalicylidene)-1,2-diaminoethane-boron complex (**3**)

The dissolved N,N'-Bis(3-tert-Butyl-5-methylsalicylidene)-1,2-diaminoethane (**2**) (0.25 g, 0.61 mmol) in dry toluene (20 mL) was degassed with argon at room temperature. After the mixture was stirred for 15 min at 60 °C in presence of triethylamine (0.85 mL, 6.1 mmol).

$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.13 mL, 9.2 mmol) was added slowly to the resulting mixture and kept for 3 h at 110 °C under argon atmosphere. The progress of the reaction was controlled with the TLC.

The finished reaction was diluted with CHCl_3 (30 mL) and rinsed with NaHCO_3 . The toluene and CHCl_3 phase was dried over Na_2SO_4 and the solvent was evaporated. The obtained raw product was purified by column chromatography on silica gel eluting with CHCl_3 /methanol-100/1 to obtain pure boron complex (**3**). Yield: 48% (145 mg). FT-IR (UATR-TWOTM) ν max/cm⁻¹: 3042 (Ar, C-H), 2951-2857 (Aliph., C-H), 1634 (C=N), 1567 (Ar, C=C), 1469-1358 (Aliph., C-C), 1182, 1044, 907, 774. $^1\text{H-NMR}$ (CHCl_3) δ (ppm): 8.25 (s, 2H), 7.37 (s, 2H), 6.96 (s, 2H), 4.30 (s, 4H), 2.23 (s, 6H), 1.43 (s, 18H).

$^{13}\text{C-NMR}$ (CHCl_3) δ (ppm): 167.92, 156.69, 137.67, 134.05, 129.75, 129.20, 115.45, 54.00, 35.09, 29.48, 20.72. UV-Vis (CHCl_3): λ_{max} (nm) (log ϵ) 242 (3.82), 276 (4.24), 376 (3.83). Anal. Calc. $\text{C}_{26}\text{H}_{34}\text{B}_2\text{F}_4\text{N}_2\text{O}_2$ (%): C, 61.94; H, 6.80; B, 4.29; F, 15.07; N, 5.56; O, 6.35; Found (%): C, 61.91; H, 6.87; N, 5.38. MS : m/z 475.3196 [M-F]⁺, m/z: 527.2576 [M+Na]⁺.

3. Results and discussion

3.1. Synthesis and characterization

The reaction steps for target compound **3** were shown in Scheme 1. In the first stage, As a first step, the reaction of 2-tertbutyl-4-methylphenol with urotropin in glacial CH_3COOH gave the aromatic aldehyde derivative (**1**) using the literature procedure by applying Duff reaction which is one of the most convenient preparation methods for *ortho*-hydroxysubstituted aromatic aldehydes [15].

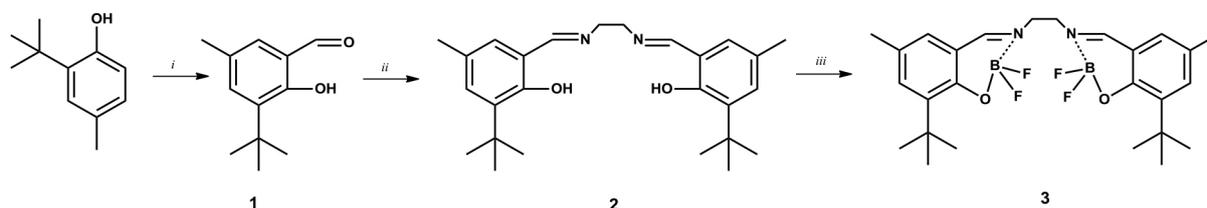
The new bis-imine ligand (**2**) was synthesized by the condensation reaction of the aldehyde derivative (**1**) and commercially available ethylenediamine in methanol at reflux temperature. Boron complexation was carried out with the reaction of **2** and $\text{BF}_3 \cdot \text{OEt}_2$ in toluene at 110 °C by using triethylamine as base to afford **3**.

The achieved pure products were characterized by spectroscopic methods such as $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, UV/Vis and FT-IR and MS and elemental analysis. The results showed that the products are in the expected structure.

When compared the FT-IR spectra of 2-tertbutyl-4-methylphenol and **1**, the formation of **1** could be diagnosed with the existence of carbonyl peak at 1645cm⁻¹ and C-H vibrations at 2895 cm⁻¹ and 2773 cm⁻¹ belonging to the aldehyde group.

The FT-IR spectrum of **2** displayed the imine vibration band at 1630 cm⁻¹ by the disappearance of the C=O stretching band indicating the condensation reaction to give **2**.

It was observed that the imine (C=N) vibration at 1630 cm⁻¹ originating from free ligand **2** shifted to 1634 cm⁻¹ upon complexation with boron. In addition, the presence of an B-O and B-N vibration peaks at 1182 and 1044 cm⁻¹ are evidence for the formation of boron complex (**3**) [17].



Scheme 1. Synthesis route: (i) glacial CH_3COOH , urotropin, 120 °C (ii) ethylenediamine, methanol (iii) TEA, $\text{BF}_3 \cdot \text{Et}_2\text{O}$, toluene

The $^1\text{H-NMR}$ data presented satisfactory results for proposed structures. When compared the $^1\text{H-NMR}$ spectra of compound **1** and **2**, the disappearances of HC=O proton signal of **1** and the appearance of peak of imine proton at 8.33 ppm shows that the imine condensation reaction has occurred. The other characteristic peak was observed at 3.91 ppm related to methylene group of **2**. The disappearance of the signal due to phenolic OH protons at 13.58 ppm arising from free ligand (**2**) is attributed to the formation of B–O bond in $^1\text{H-NMR}$ spectrum of **3**. Also, The azomethine $-\text{CH=N}-$ proton of ligand (**2**) at 8.33 ppm shifted to highfield observing at 8.25 ppm in complex (**3**), as well.

When the results obtained with $^{13}\text{C-NMR}$ are evaluated, the peaks at 167.43 ppm and 68.19 ppm belonging to the carbon atom of the imine group and the carbon atoms of the methylene group, respectively, are the characteristic proof for the occurrence of imine compound (**2**).

In the $^{13}\text{C-NMR}$ spectrum of **3**, the signals for carbon atoms of the imine ($-\text{CH=N}-$) group and the carbon atoms of the methylene group were observed at 167.94 ppm and 54.00 ppm, respectively.

The mass spectrum of **3** was gained by the electro-spray ionization mass spectrometer and the result indicated the existence of aimed product by presenting the molecular ion peak m/z : 475.3196 $[\text{M-F}]^+$ and m/z : 527.2576 $[\text{M+Na}]^+$ as seen in Figure 1.

The absorption spectra of **2** and boron complex (**3**) were performed in 1×10^{-4} M concentration of CHCl_3 solution are given in Figure 2. In the absorption spectrum of the **2**, two main absorption bands appeared at 246 and 334 nm which arised from $\pi-\pi^*/n-\pi^*$ transitions [18]. The bands resulting from same transitions showed up in the spectrum of the boron complex (**3**), as well. The UV–Vis spectrum of boron complex (**3**) in CHCl_3 solution displayed broad bands at 276 nm and 376 nm and with a shoulder at 242 nm. When compared to the free ligand (**2**), these bands appeared at a longer wavelength indicating the coordination of the boron to the ligand.

The electronic spectrum of the prepared boron complex (**3**) was also recorded in variety of solvents (THF, CHCl_3 , acetone, DMF, DMSO acetonitrile and DCM) to determine the solvent effect on its spectroscopic properties and detect the appropriate solvent for future photophysical and photochemical studies (Fig. 3)

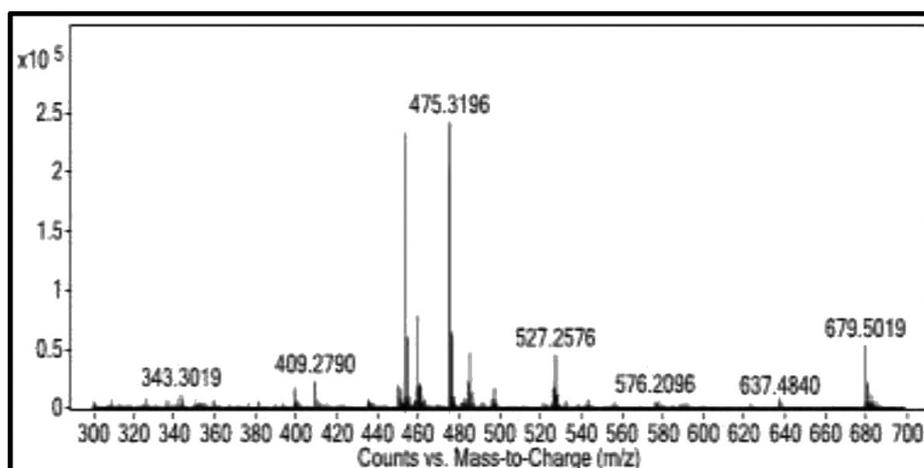


Figure 1. MS spectrum of **3**.

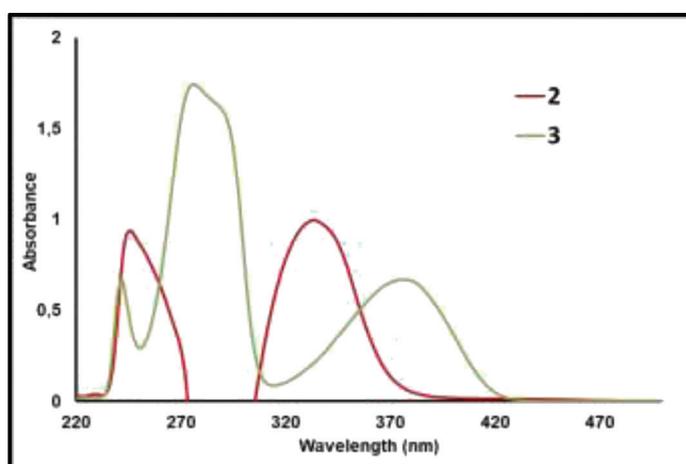


Figure 2. Absorption spectra of **2** and **3** in CHCl_3 (Concentration 1×10^{-4} mol.L $^{-1}$).

When the solvent polarity was increased among the studied solvents changing from chloroform to DMF or DMSO, it was observed hypsochromic shift (~ 10 nm) at absorptions wavelength which agree with the natural behavior of BF_2 complexes of $\text{N}^{\wedge}\text{O}$ -bidentate ligands [19].

The molar absorption coefficients (ϵ) of the prepared boron complex (**3**) are different in different solvents due to having unique solution properties (Fig. 3). While the biggest absorbance value was observed in THF, the lowest absorption was observed in acetonitrile.

The absorption spectra clearly show that the broad bands of the boron complex (**3**) were seen at the range of 366-374 nm which is responsible for the complexation. The absorption bands at 368 nm in acetone, acetonitrile and THF, at 366 nm in DMF and DMSO, at 376 nm in CHCl_3 and at 374 nm in DCM were observed for the same concentration solutions of **3**.

3.2. Fluorescence spectra

The fluorescence behavior of synthesized boron complex (**3**) was examined in a variety of solvents such as acetone, acetonitrile, CHCl_3 , DCM, DMF, DMSO and THF at room temperature. Since the susceptibility of the fluorophores towards to the solvent polarity is quite important in fluorescent field, the effect of the solvents on the fluorescence intensity was examined. It was seen that the synthesized boron complex (**3**) has similar fluorescence behavior in all solutions from the emission wavelength aspect.

The absorption and fluorescence emission, excitation spectrum of boron complex (**3**) in THF was given as an example in Figure 4. The emission shape is the mirror image of the absorption shape and this similarity of the absorption and emission spectra for all the studied solvents, suggesting that the Schiff base complex (**3**) structure was not affected by the excitation. When con-

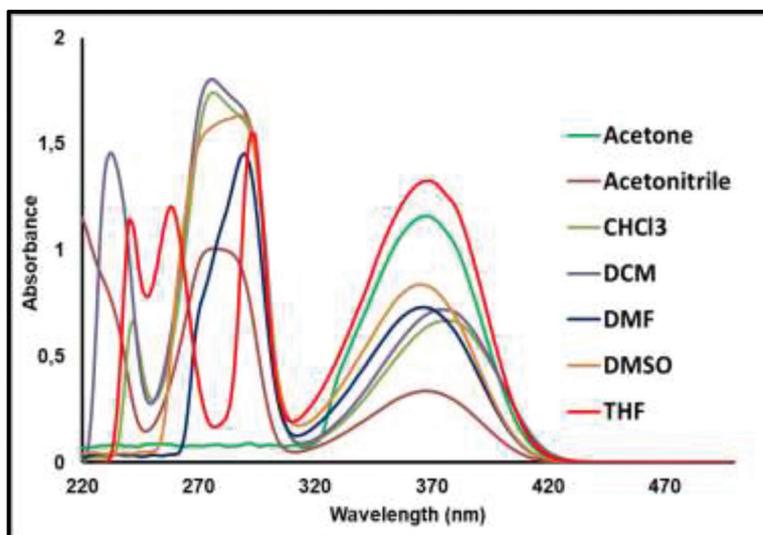


Figure 3. UV-Vis spectra of the compound **3** in acetone, acetonitrile, CHCl_3 , DCM, DMF, DMSO, and THF. (Concentration 1×10^{-4} mol.L $^{-1}$).

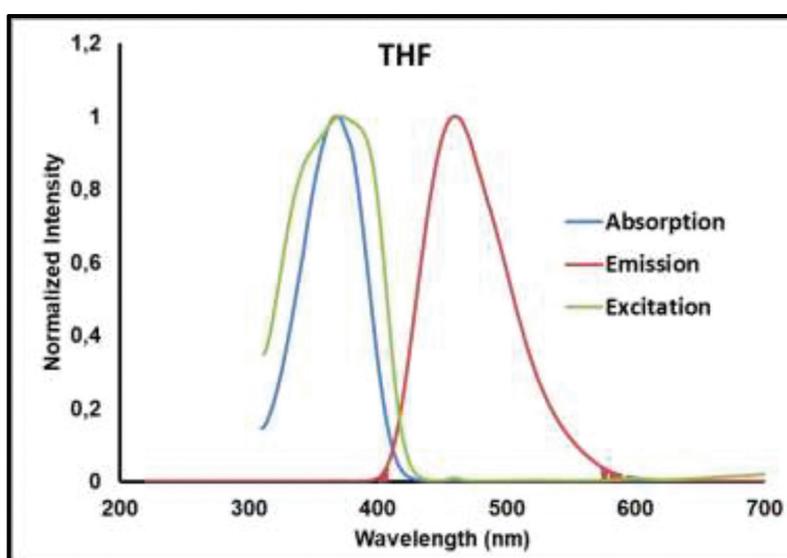


Figure 4. Absorption, excitation and emission spectra of **3** in THF. Excitation wavelength = 368 nm.

sidered the excitation spectra, it was observed slightly red-shifted up to 1-2 nm assessed as minor shift in comparison with its absorption spectra (Fig. 4).

Fluorescence emission peaks of **3** were observed at 460 nm in CHCl_3 and THF, 462 nm in acetone, 463 nm in DCM, 465 nm in acetonitrile and DMF and 466 nm in DMSO when excited at 366–376 nm. It was observed that the fluorescence emission was the highest in THF and the lowest in acetonitrile (Fig. 5).

Whereas the Schiff base ligand (**2**) itself is non-emissive and after complexation with the BF_2 unit, the fluorescence efficiencies of the obtained boron complex (**3**) significantly increased. The introduction of the BF_2 to the free ligand may be increased the rigidity and this resulted in an increase in emission efficiency [20].

Stokes shifts were calculated by taking into consideration the difference between absorption and emission wavelength. The determined Stokes shifts are 84 nm in CHCl_3 , 89 nm in DCM, 92 nm in THF, 94 nm in acetone, 97 nm in acetonitrile, 99 nm in DMF and 100 nm in DMSO and these results were similar to typical of bi-metallic fluoroborates derivatives [13]. The observed large Stokes shifts could be resulted from the presence of an excited-state intramolecular charge transfer (ICT) [21].

3.3. Fluorescence quantum yields (Φ_F)

Fluorescence quantum yields (Φ_F) of boron complex **3** have been measured in various solvents by the comparative method using Eq. (1): [22].

$$\Phi_F = \Phi_{F(\text{Std})} \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2} \quad \text{Eq. (1)}$$

where F and F_{Std} are the areas under the emission profile of the boron complex (**3**) and the standard,

respectively. A and A_{Std} are the absorbances of the sample and standard corresponding to excitation wavelengths, and n^2 and n_{Std}^2 are refer to refractive indices of solvents ($n_{\text{acetone}}: 1.36$, $n_{\text{acetonitrile}}: 1.34$, $n_{\text{chloroform}}: 1.44$, $n_{\text{DCM}}: 1.42$, $n_{\text{DMF}}: 1.43$, $n_{\text{DMSO}}: 1.48$, $n_{\text{THF}}: 1.41$) in prepared solutions for the sample and standard, respectively. Quinine sulfate ($\Phi_F = 0.54$ in 0.1 M H_2SO_4) was utilized as standard [23]. The absorbances of the solutions were adjusted to be between 0.04 and 0.05.

Fluorescence quantum yield (Φ_F) values were achieved in various solvents such as acetone, acetonitrile, CHCl_3 , DCM, DMF, DMSO and THF at room temperature in order to observe the effect of solvent. The same excitation wavelength in which the solution of **3** is measured was applied for the standard for comparison purposes.

The results of quantum yield were determined to be in the range of 0.40-0.48 in the studied solvents as similar to each other, except for in acetonitrile; in acetone 0.41, in CHCl_3 0.43, in DCM 0.48, in DMF 0.47, in DMSO 0.47, in THF 0.40 and in acetonitrile 0.30 (Table 1).

As a result of comparison of these results, the lowest value was obtained in acetonitrile while the obtained highest value in DCM. When compared the some reported BF_2 complexes [19], the quantum yields of complex **3** studied in this work are higher in solution, comparatively. However, fluorescence quantum yield (Φ_F) values studied in all solutions lower than standard. The limiting effect on quantum yield can be explained by the increase in energy transfer through intersystem crossing (ISC) [24].

The absorption maxima, absorption coefficients, emission maxima, Stokes shifts and quantum yields are summarized in Table 1.

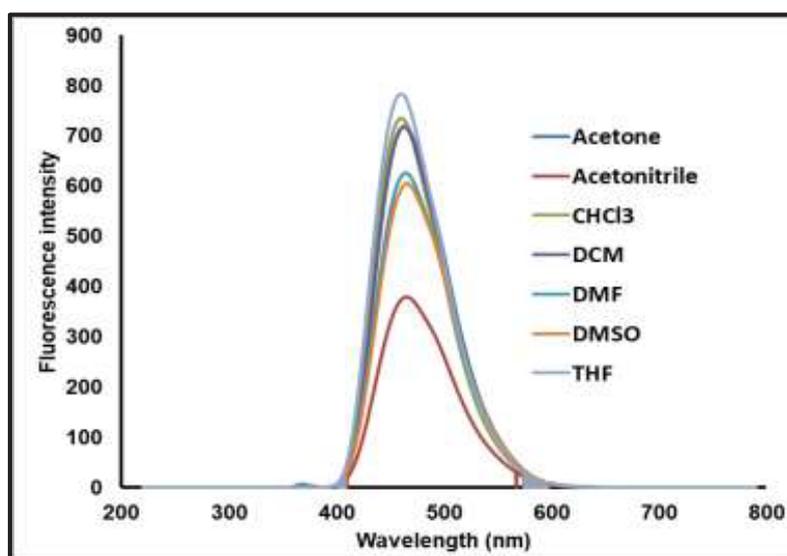


Figure 5. Emission profile of compound **3** in different solvents. (Concentration: 1×10^{-4} M).

Table 1. Absorption, excitation, emission spectral data and absorption coefficient for compound **3**.

Solvent	λ_{\max} (nm)	log ϵ	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes Shift Δ_{Stokes} (nm)	Φ_{F}
Acetone	368		368	462	94	0.41
Acetonitrile	276, 368		368	465	97	0.30
CHCl ₃	276, 376	4.24, 3.83	376	460	84	0.43
DCM	276, 374		374	463	89	0.48
DMF	290, 366		366	465	99	0.47
DMSO	288, 366		366	466	100	0.47
THF	294, 368		368	460	92	0.40

4. Conclusion

In this study, a new Schiff base-boron complex **3** was reported together with its synthesis and characterization for the first time. The fluorescence and absorption properties were studied in different solvents in order to see the effect of solvent diversity on spectral properties. Complex **3** was found to be highly emissive fluorophore and emits blue fluorescence with an emission maximum within the range of 460–466 nm depending on the solvent polarity. The resulting complex displayed large Stokes shifts (89–100 nm) and the highest Stokes shift (100 nm) was reached with the solution prepared in DMSO. In addition to exhibiting high Stokes shift, relatively high fluorescent quantum yields of 30–48% in solutions were obtained. In the light of these results, among studied solvents, boron complex **3** can be used as potential for both organic emitters and imaging reagent in DMSO.

References

- Treibs A., Kreuzer F.H., Difluorboryl komplexe von di und tripyrrylmethenen, *Justus Liebigs Ann. Chem.*, 718, 208–223, 1968.
- Burghart A., Kim H., Welch M.B., Thoresen L. H., Reibenspies J., Burgess K., 3, 5-Diaryl-4, 4-difluoro-4-bora-3a, 4a-diaza-s-indacene (BODIPY) dyes: synthesis, spectroscopic, electrochemical, and structural properties, *J. Org. Chem.*, 64, 7813–7819, 1999.
- Liu Y., Guo J., Zhang H., Wang Y., Highly efficient white organic electroluminescence from a double-layer device based on a boron hydroxyphenylpyridine complex, *angew. Chem. Int. Ed.* 41, 182–184, 2002.
- Maar R.R., Barbon S.M., Sharma N., Groom H., Luyt L.G., Gilroy J.B., Evaluation of anisole-substituted boron difluoride formazanate complexes for fluorescence cell imaging, *Chem. Eur. J.* 21, 15589–15599, 2015.
- Kowada T., Maeda H., Kikuchi K., BODIPY-based probes for the fluorescence imaging of biomolecules in living cells, *Chem. Soc. Rev.*, 44, 4953–4972, 2015.
- Kamkaew A., Lim S.H., Lee H.B., Kiew L.V., Chung L.Y., Burgess K., BODIPY dyes in photodynamic therapy, *Chem. Soc. Rev.*, 7, 42 (1), 77–88, 2013.
- Moon S.Y., Cha N.R., Kim Y.H., Chang S., New Hg²⁺-selective chromo- and fluoroionophore based upon 8-hydroxyquinoline. *J. Org. Chem.*, 69, 181–183, 2004.
- Hawthorne M.F., The role of chemistry in the development of boron neutron capture therapy of cancer, *Angw. Chem. Int. Ed. Engl.*, 32, 950–984, 1993.
- Qiao F., Liu A., Zhou Y., Xiao Y., Yang P.O., Bulk heterojunction organic solar cell based on a novel fluorescent fluorine–boron complex, *J. Mater. Sci.*, 44, 1283–1286, 2009.
- Tamgho I., Hasheminasa A., Engle J.T., Nemykin V.N., Ziegler C.J., A new highly fluorescent and symmetric pyrrole-BF₂ chromophore: BOPHY, *J. Am. Chem. Soc.*, 136, 5623–5626, 2014.
- Yu C., Zhang L.J.P., Feng Z., Cheng C., Wei Y., Mu X., Hao E., Highly fluorescent BF₂ complexes of hydrazine–schiff base linked bispyrrole, *Org. Lett.*, 16, 3048–3051, 2014.
- Zhang H., Huo C., Zhang J., Zhang P., Tian W., Wang Y., Efficient single-layer electroluminescent device based on a bipolar emitting boron-containing material, *Chem. Commun.*, 3, 281–283, 2006.
- Guieu S., Cardona F., Rochab J., Silva A.M.S., Luminescent bi-metallic fluoroborates derivatives of bulky Salen ligands, *New. J. Chem.*, 38, 5411–5414, 2014.
- Perrin D.D., Armarego W.L.F., Perrin D.R. Purification of laboratory chemicals, New York: Pergamon Press, 2013.
- Larrow J.F., Jacobsen E.N., A practical method for the large-scale preparation of [N,N'-Bis(3,5-ditertbutylsalicylidene)-1,2-cyclohexanediaminato(2-)] manganese(III) chloride, a highly enantioselective epoxidation catalyst, *J. Org. Chem.*, 59, 1939–1942, 1994.
- Sen P., Kansiz S., Golenyac I.A., Dege N., Crystal structure and Hirshfeld surface analysis of N,N'-bis(3-tert-butyl-2-hydroxy-5-methylbenzylidene) ethane-1,2-diamine, *Acta Cryst. E74*, 1147–1150, 2018.
- Kilic A., Kayan C., Aydemir M., Durap F., Durgun M., Baysal A., Tas E., Gumgum B., Synthesis of new boron complexes: Application to transfer hydrogenation of acetophenone derivatives, *Appl. Organometal. Chem.*, 25, 390–394, 2011.
- Lever A.B.P., *Inorganic Electronic Spectroscopy*, second ed., Elsevier Science, Amsterdam, 1984.
- Frath D., Azizi S., Ulrich G., Retailleau P., Ziesel R.,

- Facile synthesis of highly fluorescent boranil complexes, *Org. Lett.*, 13, 3414-3417, 2011.
- [20] Ren Yi., Liu X., Gao W., Xia H., Ye L., Mu Y., Boron complexes with chelating anilido-imine ligands: Synthesis, structures and luminescent properties, *Eur. J. Inorg. Chem.*, 2007, 1808–1814, 2007.
- [21] Peng X., Song F., Lu E., Wang Y., Zhou W., Fan J., Gao Y., Heptamethine Cyanine Dyes with a Large Stokes Shift and Strong Fluorescence: A Paradigm for Excited-State Intramolecular Charge Transfer, *J. Am. Chem. Soc.*, 127, 4170-4171, 2005.
- [22] Sen P., Atmaca G.Y., Erdogmus A., Kanmazalp S.D., Dege N., Yildiz S.Z., Peripherally tetra-benzimidazole units-substituted zinc(II) phthalocyanines: Synthesis, characterization and investigation of photophysical and photochemical properties, *J. Lumin.*, 194, 123-130, 2018.
- [23] Lugovik K.I., Eltyshev A.K., Suntsova P.O., Smoluk L.T., Belousova A.V., Ulitko M.V., Minin A.S., Slepukhin P.A., Benassi E., Belskaya N.P., Fluorescent boron complexes based on new N,O-chelates as promising candidates for flow cytometry, *Org. Biomol. Chem.*, 16, 5150–5162, 2018.
- [24] Sen P., Atmaca G.Y., Erdoğan A., Dege N., Genç H., Atalay Y., Yildiz S. Z., The synthesis, characterization, crystal structure and photophysical properties of a new meso-BODIPY substituted phthalonitrile, *J. Fluoresc.* 25, 1225-1234, 2015.