



REGULAR ARTICLE

A highly fluorescent tri-nuclear boron complex with large Stokes shifts based on tripodal Schiff base: synthesis and photophysical properties

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Abstract. In this study, a new imine-based tripodal ligand and its difluoroboron complex were designed and synthesized. This trinuclear-boron complex was prepared for the first time and fully characterized by common spectroscopic techniques such as $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FT-IR, UV-Vis and MS analysis. The optical and fluorescence properties of complex were examined in CHCl_3 , THF, acetonitrile, EtOAc, DMF and DMSO. It was revealed that the obtained boron complex showed intense emission with large Stokes shifts in the range from 83 nm to 96 nm. As a result of quantification of fluorescence quantum yields, it has been observed that it has high quantum yield values up to 48%. The large Stokes shifts and high efficient emissions in the solutions of boron complex make it precious fluorophore for potential applications in materials science.

Keywords. Synthesis; Difluoroboron complex; tripodal ligand; fluorescence property; Stokes' shift; quantum yield; fluorescence lifetime.

1. Introduction

Fluorescent dyes have drawn significant interest increasingly for many fields such as fluorescence imaging and labeling,^{1,2} light-emitting diodes,³ fluorescent chemosensors for ions and neutral analytes for the detection of chemically and/or environmentally important species.⁴

BF_2 complexes of dipyrromethene (BODIPY), known as one of the most main fluorescent dyes, form the class of organic fluorine boron complexes. They have exceptional photophysical properties presenting intense fluorescence emission peaks with high quantum yields and chemical and photo-durability.⁵ In addition to the use as a fluorescent material, these properties of BODIPYs have been also found to be valuable for some applications such as photodynamic therapy as a photosensitizer,⁶ solar cells,⁷ electrochromic display systems.⁸ However, BODIPY derivatives mostly show small Stokes shift.

Recent demands focused on obtaining new boron-containing fluorescent dyes that can provide promising

optical properties with large Stokes shift which is a very important feature of a fluorophore. Thus, they could be used as a material in many fields. For this purpose, in addition to dipyrromethene derivatives, benzimidazoles,⁹ hydrazine-bispyrrole (BOPHY),¹⁰ anilido-imine¹¹ ligands have been studied as the N,N-chelated difluoroboron complexes because of the promising luminescent properties so far. Among the compounds studied with this aim, BF_2 complexes of Schiff-base ligands have been presented in a few studies as the N,O-chelated difluoroboron complexes.¹² Schiff base ligands can form stable complexes with most metals and, therefore the design and synthesis of Schiff base ligands in coordination chemistry are crucial.¹³

However, while the most fluorophores show intense fluorescence in solution, they display weak fluorescence emission in the solid state resulting from the self-quenching of the fluorophore. This deficiency limiting its use as a material for practical applications can be attributed to the planarity of the most dyes.¹⁴

In this study, a new trinuclear boron complex was designed and synthesized in order to obtain an emissive

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molecule possessing large Stokes shift to overcome the mentioned challenge.

The condensation of an aromatic aldehyde derivative with tris(2-aminoethyl)amine (tren) in a 3:1 ratio resulted in a Schiff base structure called tripodal backbone with ternary imine group. The synthesis and characterization of its boron complex $(BF_2)_3L$ (**3**) as flexible fluorophore with three BF_2 units was performed. To the best knowledge, there are a few examples on the tripodal ligand-like and their metal complexes in the literature.^{15–17}

The optical and fluorescence properties of the prepared tris-metallic boron complex (**3**) were also investigated. It was observed that the obtained chromophore showed high blue fluorescence in solution with a large Stokes shift.

2. Experimental

2.1 Chemicals and instruments

2-tertbutyl-4-methylphenol, urotropin, glacial acetic acid, tris (2-aminoethyl), chloroform ($CHCl_3$), ethylacetate (EtOAc), methanol, ethanol (EtOH), dichloroethane, N,N-diisopropylethylamine (DIPEA), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), acetonitrile, boron trifluoride diethyl etherate $BF_3 \cdot O(Et)_2$, $NaHCO_3$ were obtained from Sigma-Aldrich. All solvents were dried and purified according to the procedures given by Perrin and Armarego¹⁸ before using. Thin layer chromatography (TLC) based on silica gel 60-HF254 as an adsorbent was applied for monitoring the progress of the reactions and chemical purity of the compounds. Silica gel (Merck grade 60) was used at column chromatography. 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. 1H and ^{13}C NMR spectra were carried out with Bruker AVANCE 600 MHz NMR Spectrometer and Varian Mercury Plus 300 MHz spectrometer. Mass analysis was performed on Bruker microTOF. Fluorescence lifetimes were measured using a time-correlated single photon counting setup (TCSPC) (FluoTime 200, Picoquant GmbH) with a diode laser (LDH-P-670 with PDL 800-B, Picoquant GmbH, 670 nm, 20 MHz repetition rate, 44 ps pulse width).

2.2 Synthesis

The synthesis of 3-tert-Butyl-2-hydroxy-5-methylbenzaldehyde (**1**) was accomplished according to the reported work.¹⁷ The spectroscopic results are consistent with the literature.

2.2a Synthesis of Ligand (2): In a 100 mL flask, tris (2-aminoethyl) amine (0.102 mL, 0.68 mmol) was

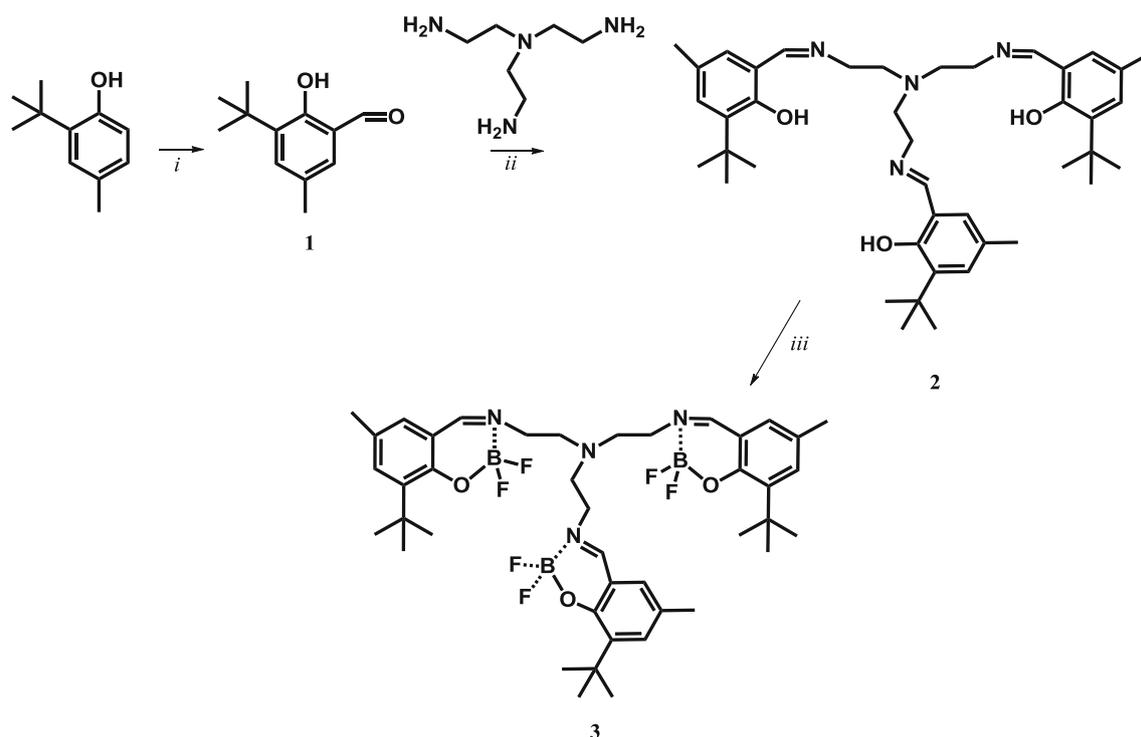
dissolved in 20 mL ethanol at 50 °C. 3-tert-butyl-2-hydroxy-5-methylbenzaldehyde (**1**) (0.39 g, 2.043 mmol) was dissolved in 20 mL of ethanol and added into mixture dropwise. The reaction mixture was degassed by argon-vacuum system. The reaction temperature was adjusted to boiling temperature and stirred under reflux for 6 h. The course of the reaction was checked by TLC (chloroform-EtOAc 10/1). After the reaction was completed, the solution was evaporated to 1/3 volume. The precipitated product was filtered off, washed with ethanol and dried in a vacuum desiccator. Yield: 92% (0.415 g). FT-IR (UATR-TWOTM) ν max/cm⁻¹: 3040 (Ar, C-H), 2947–2810 (Aliph., C-H), 1631 (C = N), 1594 (Ar, C = C), 1437–1357 (Aliph., C-C), 1264, 1046, 842, 783. 1H -NMR ($CHCl_3$) δ (ppm): 7.63 (s, 3H), 7.09 (d, 3H), 5.41 (s, 3H), 3.49–3.47 (t, 6H), 2.84–2.81 (t, 6H), 2.03 (s, 9H), 1.43 (s, 27H). ^{13}C -NMR ($CHCl_3$) δ (ppm): 167.07, 158.27, 136.68, 130.47, 130.06, 126.42, 118.64, 58.38, 56.38, 34.90, 29.64, 20.54. UV-Vis (DMSO): λ max (nm) (log ϵ) 266 (4.25), 330 (3.83). MS (MALDI-TOF): m/z 670.128 $[M+1]^+$, 692.155 $[M+Na]^+$.

2.2b Synthesis of $L(BF_2)_3$ Complex (3): In a 100 mL round bottom flask, DIPEA (0.8 mL) was added to a stirred solution of ligand (**2**) (0.2 g, 0.3 mmol) in dry dichloroethane (30 mL) and degassed with argon at room temperature. After the mixture was stirred for 15 min at 60 °C, $BF_3 \cdot O(Et)_2$ (0.6 mL, 4.5 mmol) was added slowly to the resulting mixture and kept for 3 h at 85 °C under argon atmosphere. The course of the reaction was monitored with TLC (chloroform-EtOH 5/1). The completed reaction was diluted with $CHCl_3$ (40 mL) and quenched by adding $NaHCO_3$ solution. The mixture was extracted with $CHCl_3$ (3 \times 15 mL). The $CHCl_3$ phase was dried over Na_2SO_4 and the solvent was evaporated to dryness. The obtained crude product was purified by column chromatography on silica gel eluting with $CHCl_3$ /methanol-100/1 to obtain pure boron complex (**3**). Yield: 42% (0.102 g). FT-IR (UATR-TWOTM) ν max/cm⁻¹: 3012 (Ar, C-H), 2955–2857 (Aliph., C-H), 1642 (C = N), 1568 (Ar, C = C), 1446–1363 (Aliph., C-C), 1245, 1120, 1024, 945, 823. 1H -NMR (DMSO) δ (ppm): 8.43 (s, 3H), 7.41 (d, 3H), 6.58 (s, 3H), 3.77 (t, 6H), 2.96 (t, 6H), 2.13 (s, 9H), 1.36 (s, 27H). ^{13}C -NMR (DMSO) δ (ppm): 167.17, 155.20, 138.40, 136.62, 129.57, 128.81, 115.81, 52.89, 50.82, 34.85, 29.42, 20.38. ^{11}B ($BF_3 \cdot O(Et)_2$, $CDCl_3$): δ 0.382 (t). UV-Vis (DMSO): λ max (nm) (log ϵ) 276 (4.72), 362 (4.19). MS (MALDI-TOF): m/z 794.336 $[M-F]^+$, 835.372 $[M+Na]^+$, 852.356 $[M+Na+H_2O]^+$.

3. Result and Discussion

3.1 Synthesis and spectroscopic characterization

As a first step, 3-tert-Butyl-2-hydroxy-5-methylbenzaldehyde (**1**) was obtained from the reaction of 2-tert-butyl-4-methylphenol with urotropine in glacial



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

CH_3COOH by applying Duff reaction method which is the procedure to obtain aldehyde in the *ortho*-position of aromatic phenols.¹⁹ In the second step, the condensation reaction was performed between the aldehyde derivative (1) and tris (2-aminoethyl) amine in anhydrous ethanol at reflux temperature to give the ligand (2) providing N,O-chelating. Finally, the formation of the trinuclear fluoroborate complex was carried out with the reaction of 2 and $\text{BF}_3 \cdot \text{O}(\text{Et})_2$ in dry dichloroethane at 85 °C by using DIPEA as a base to afford 3.

The structural characterization of the achieved pure products was performed by spectroscopic methods such as $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, UV/Vis and FT-IR and MS analysis. The spectroscopic results confirmed the expected structures.

In the FT-IR spectrum of 2, the formation of tris imine was verified the disappearance of the carbonyl band at 1645 cm^{-1} originating from 1 and the existence of $-\text{C} = \text{N}$ vibration band at 1631 cm^{-1} . The FT-IR spectra of triboron complex (3), the most significant differences were that the imine ($\text{C} = \text{N}$) and Ar-O-H vibrations at 1631 cm^{-1} and 1264 cm^{-1} arising from free ligand 2 shifted to 1642 cm^{-1} and 1245 cm^{-1} upon complexation with boron. These results indicate that phenolic protons and imines are involved in coordination with boron. Besides, the presence of B-O and B-N vibration peaks at 1180 cm^{-1} and 1024 cm^{-1} are evidence for the formation of boron complex (3).

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra have provided satisfactory information confirming the proposed structure.

When the $^1\text{H-NMR}$ spectra of compounds 1 and 2 are compared, the disappearances of $\text{HC} = \text{O}$ proton signal of 1 shows that the imine condensation reaction has taken place. The $^1\text{H-NMR}$ spectra obtained for 2 and 3, the absence of OH proton signal of ligand (2) was the evidence that the boron complexation was occurred to give triboron complex 3. In the $^1\text{H-NMR}$ spectra of the newly synthesized compounds, the aromatic protons were observed between 7.63–7.09 ppm for compound 2 and 7.41–6.58 ppm for compound 3. The azomethine $-\text{CH} = \text{N}-$ proton of complex (3) arose at 8.43 ppm. The aliphatic protons belonging to the $-\text{CH}_3$ groups on the benzene ring were in the range of 2.03–1.43 ppm for compound 2 and 2.13–1.36 ppm for compound 3. The $^{11}\text{B-NMR}$ signals were obtained at 0.382 ppm that is in accordance with sp^3 boron.

When the $^{13}\text{C-NMR}$ spectra of the obtained structures are examined, the formation of imine condensation was approved by the absence of $\text{HC} = \text{O}$ carbon signal of 1. The observed signals for carbon atoms of the imine ($-\text{CH} = \text{N}-$) groups were 167.07 ppm and 167.17 ppm for compounds 2 and 3, respectively.

The mass spectrum of 2 and 3 was obtained by the MALDI-TOF Mass spectrometer confirming the proposed structures. In the mass spectrum of 2 the molecular ion peak and Na-adducted peak were observed at

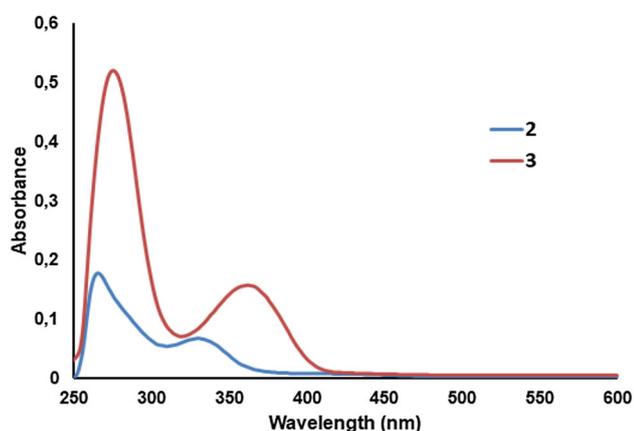


Figure 1. Absorption spectra of **2** and **3** in DMSO (Concentration $1 \times 10^{-5} \text{ mol.L}^{-1}$).

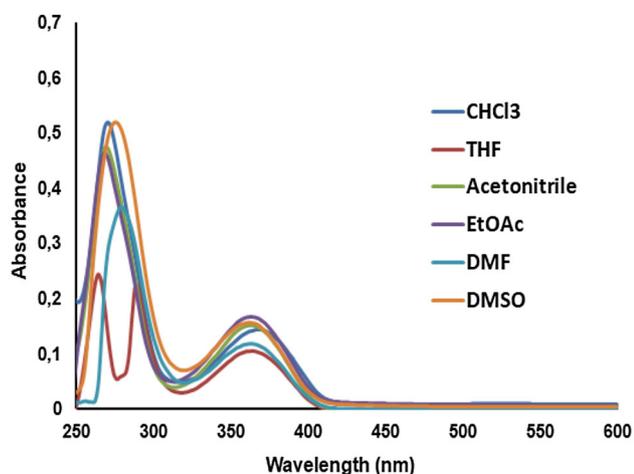


Figure 2. UV-Vis spectra of the compound **3** in CHCl_3 , THF, acetonitrile, EtOAc, DMF, DMSO (Concentration $1 \times 10^{-5} \text{ mol.L}^{-1}$).

$670.128 [\text{M} + 1]^+$, $692.155 [\text{M} + \text{Na}]^+$. The observed main peaks for compound **3** were determined at $794.336 [\text{M} - \text{F}]^+$, $835.372 [\text{M} + \text{Na}]^+$, $852.356 [\text{M} + \text{Na} + \text{H}_2\text{O}]^+$.

The UV-Vis absorption spectrum of **2** was recorded together with the triboron complex (**3**) at a concentration of $1 \times 10^{-5} \text{ M}$ DMSO solution, as comparatively (Figure 1). In the absorption spectrum of the **2**, two main absorption bands appeared at 266 and 330 nm which arises from $\pi - \pi^*/n - \pi^*$ transitions.²⁰

The triboron complex (**3**) showed good solubility in common organic solvents. For this reason, the electronic spectrum of the synthesized boron complex (**3**) was recorded in solutions prepared with different solvents (CHCl_3 , THF, acetonitrile, EtOAc, DMF, DMSO) to see the effect of solvent difference on its spectroscopic properties at room temperature (Figure 2).

Absorptions of triboron complex (**3**) were observed at 270 and 368 nm in CHCl_3 , 288 and 364 nm in THF, 270

and 364 nm in acetonitrile, 268 and 364 nm in EtOAc, 280 and 362 nm in DMF, 276 and 362 nm in DMSO at concentration of $1 \times 10^{-5} \text{ M}$ solutions (Table 1). When the obtained results among the studied solvents are compared for boron complex (**3**), it was observed that the increased solvent polarity led to absorption in the higher energy region (2–4 nm) in accordance with the natural behavior of BF_2 complexes of N O -bidentate ligands.²¹ This could be attributed that the improved dipolar characteristics reduce the transition energy of the species.²² However, the maximum absorption wavelength values that are not very different can be explained by the fact that the molecule is not much affected by the solvent polarity and the dipole moments of the molecules in their ground and excited states were almost equal.²³

The molar absorption coefficient of **3** was observed with minor differences in different solvents and the highest value was observed in the EtOAc solution.

3.2 Photophysical properties

The fluorescence behavior of the boron complex (**3**) was measured at room temperature in CHCl_3 , THF, acetonitrile, EtOAc, DMF and DMSO to observe the effect of solvents on fluorescence intensity depending on the polarity of molecular medium, since the sensitivity of the fluorophores to solvent polarity was very important in the fluorescence field.

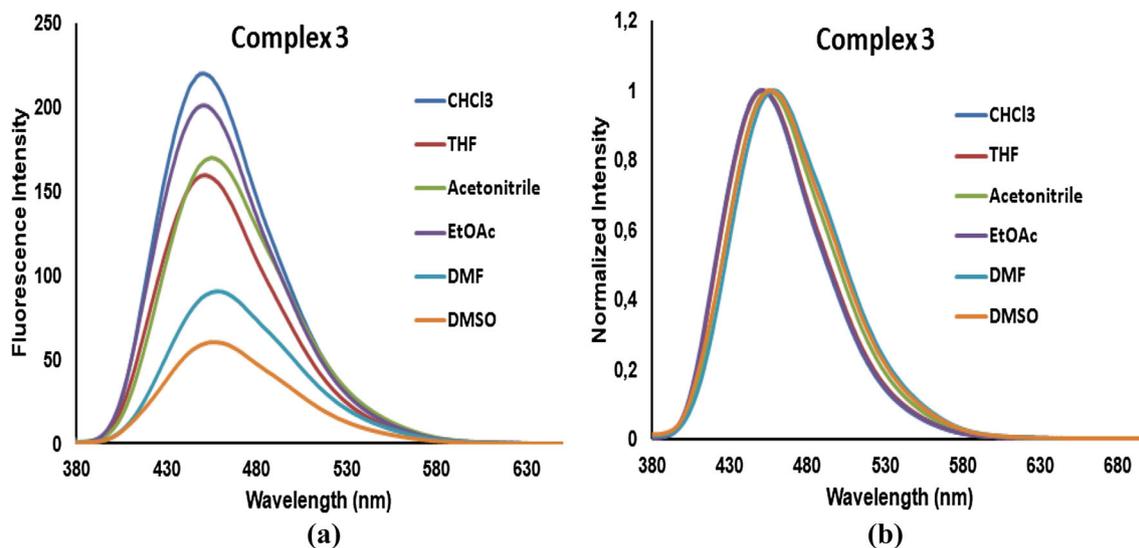
Boron difluoride complex (**3**) showed similar spectral action in terms of emission wavelength in all studied solutions and, exhibited blue fluorescence with emission maxima of 450 nm in EtOAc, 451 nm in CHCl_3 and THF, 455 nm in acetonitrile, 456 nm in DMSO when excited at their absorption maxima. As shown in Figure 3, the complex **3** showed the longest emission band with a peak at 458 nm in DMF.

The emission wavelength of this complex (**3**) significantly shifted to the red region of the spectrum when compared to the absorption wavelength. As a result of the coordination of the boron to the ligand, the bonding of the lone-pair of electrons of N atom on the ligand to the B atom reduces the energy gap between the π and π^* of the ligand. This phenomenon makes the complex more stable and increases emission efficiency, as indicated in previous studies for boron difluoride complexes.²⁴

This compound also demonstrated large Stokes shifts up to 96 nm. Stokes shifts were calculated by considering the difference between absorption and emission wavelength. The observed Stokes shifts are 83 nm in CHCl_3 , 86 nm in EtOAc, 87 nm in THF, 91 nm in acetonitrile, 94 nm in DMSO and 96 nm in DMF. It was recorded as very high compared to existing

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

Solvent	λ_{\max} (nm)	$\log \epsilon$	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes Shift Δ_{Stokes} (nm)	Φ_{F}	τ_{T} (μs)
CHCl_3	270, 368	4.71, 4.16	369	451	83	0.49	3.02
THF	288, 364	4.35, 4.02	367	451	87	0.42	2.52
Acetonitrile	270, 364	4.67, 4.17	367	455	91	0.47	2.58
EtOAc	268, 364	4.66, 4.22	367	450	86	0.48	2.72
DMF	280, 362	4.56, 4.06	368	458	96	0.35	2.25
DMSO	276, 362	4.72, 4.19	367	456	94	0.30	2.14

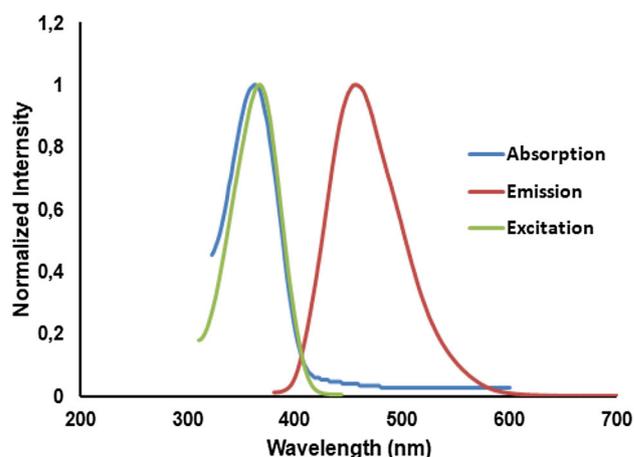
**Figure 3.** (a) Emission spectrum of compound **3** in different solvents (Concentration: 1×10^{-5} M), (b) Normalized emission spectrum of compound **3** in different solvents.

commercial fluorescent dyes.²⁵ The enlarged large Stokes shifts could be attributed to the presence of bulky side groups reducing the intermolecular $\pi - \pi$ stacking.²⁶

The absorption and fluorescence emission, the excitation spectrum of boron complex (**3**) in DMSO is given as an example in Figure 4. The excitation spectrum of compound **3** was similar to absorption spectra and both were mirror images of the fluorescence emission spectra (Figure 4). However, the excitation spectra of compound **3** are slightly red-shifted (1–5 nm) which is an inconsiderable shift in relation to its absorption spectra (Figure 4). Thus, it could be proposed that the boron complex (**3**) is not affected by the excitation in studied solutions.

3.2a Determination of fluorescence quantum yields and lifetimes: Fluorescence quantum yields (Φ_{F}) of boron complex **3** have been measured in various solvents by the comparative method using Eq. (1).²⁷

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

**Figure 4.** Absorption, excitation and emission spectra of **3** in DMSO. (Excitation wavelength = 362 nm).

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 referred to refractive indices of utilized

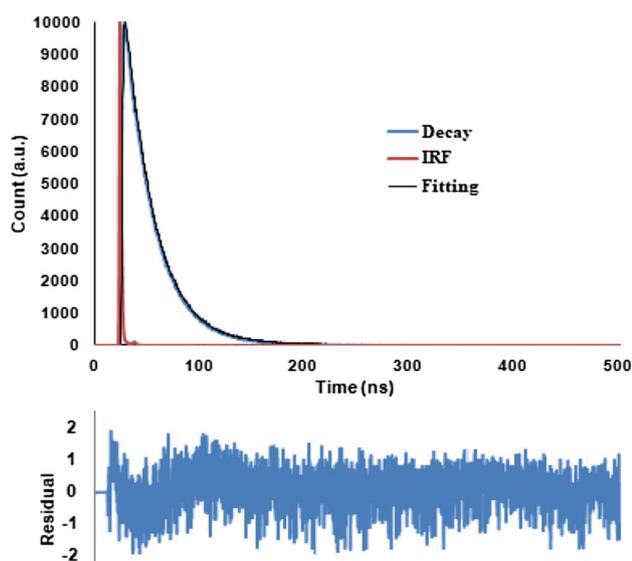


Figure 5. Fluorescence decay (blue), χ^2 fitting (black) and IRF (red) curves for complex **3** in DMSO.

solvents ($n_{\text{acetonitrile}} : 1.34$, $n_{\text{chloroform}} : 1.44$, $n_{\text{EtOAc}} : 1.37$, $n_{\text{DMF}} : 1.43$, $n_{\text{DMSO}} : 1.48$, $n_{\text{THF}} : 1.41$) in solutions for the sample and standard, respectively. Quinine sulfate ($\Phi_F = 0.54$ in 0.1 M H_2SO_4) was employed as standard.²⁸

The fluorescence quantum yields of **3** were determined in distinct organic solvents at room temperature and the obtained data were summarized in Table 1.

It was determined that the values of quantum yield were in the range of 0.30–0.49 in the studied solvents; in CHCl_3 0.49, in THF 0.42, in acetonitrile 0.47, in EtOAc 0.48, in DMF 0.35 and in DMSO 0.30 (Table 1).

The energy of the emitted state is known to depend on the solvent feature. The significantly increased quantum efficiency of complex **3** was obtained in CHCl_3 solution. Lowest fluorescence quantum yield value of boron complex **3** was obtained in DMSO solution due to the intramolecular rotation induced non-radiative process.²⁹ This phenomenon is consistent with the fluorophores which exhibit diminished quantum yield in solvents of high polarity.³⁰

TCSPC (time-correlated single photon counting) method was employed to determine the fluorescence lifetimes (τ_F) of the boron complex **3** in DMSO. Fluorescent lifetimes indicate the time that a fluorophore stays before it returns to the excited state. Fluorescence quantum yields and fluorescence lifetimes show parallel trends in dependence on the solvent.³¹ The τ_F of the boron complex **3** were determined at the range of 2.14–3.02 μs depending on solvents used. The spectroscopic and lifetime results indicate that the fluorescent behavior of **3** depends on the variety of solvents.³² The

fluorescence decay curves demonstrate an example for complex **3** in Figure 5.

4. Conclusions

In this study, the newly synthesized trinuclear difluoroboron complex (**3**) of Schiff base tripodal ligand (**2**) was reported. The boron complex (**3**) was well-characterized by spectroscopic methods and the absorption and photophysical properties were investigated in different solvents in order to determine the appropriate solvent for future applications. The measurements depending on the variety of solvents showed that complex **3** is very emissive fluorophore with an emission within the range of 450–458 nm in the solutions with large Stokes shifts (83–96 nm). Boron complex (**3**) displayed relatively high quantum yields of 30–49% in organic solvents. In the light of these results, the presented new boron complex (**3**) could be employ as a new generation blue-emitting molecule with large Stokes shift and high efficient emission in the field of fluorescence materials.

Supplementary Information (SI)

FT-IR (S1 and S5), ^1H NMR (S2 and S6), ^{13}C NMR (S3 and S7) and mass spectra (S4 and S8) applied to characterize the structure of new molecules which are synthesized are presented in supporting information at www.ias.ac.in/chemsci.

References

- Hussain T and Nguyen Q T 2014 Molecular imaging for cancer diagnosis and surgery *Adv. Drug Delivery Rev.* **66** 90
- Rao J, Dragulescu-Andrasi A and Yao H 2007 Fluorescence imaging in vivo: recent advances *Curr. Opin. Biotechnol.* **18** 17
- Chou P and Chi Y 2007 Phosphorescent dyes for organic light-emitting diodes *Chem. Eur. J.* **13** 380
- Wu D, Sedgwick A C, Gunnlaugsson T, Akkaya E U, Yoon J and James T D 2017 Fluorescent chemosensors: the past, present and future *Chem. Soc. Rev.* **46** 7105
- Loudet A and Burgess K 2007 BODIPY dyes and their derivatives: syntheses and spectroscopic properties *Chem. Rev.* **107** 4891
- Kamkaew A, Lim S H, Lee H B, Kiew L V, Chung L Y and Burgess K 2013 BODIPY dyes in photodynamic therapy *Chem. Soc. Rev.* **7** 77
- Qiao F, Liu A, Zhou Y, Xiao Y and Yang P O 2009 Bulk heterojunction organic solar cell based on a novel fluorescent fluorine–boron complex *J. Mater. Sci.* **44** 1283
- Cihaner A and Algi F 2008 A new conducting polymer bearing 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene

- (BODIPY) subunit: synthesis and characterization *Electrochim. Acta* **54** 786
- Li X, Tang P, Yu T, Sub W, Li Y, Wang Y, Zhao Y and Zhang H 2019 Two N,N-chelated difluoroboron complexes containing phenanthroimidazole moiety: synthesis and luminescence properties *Dyes Pigm.* **163** 9
 - Tamgho I, Hasheminasa A, Engle J T, Nemykin V N and Ziegler C J 2014 A new highly fluorescent and symmetric pyrrole-BF₂ chromophore: BOPHY *J. Am. Chem. Soc.* **136** 5623
 - Liu X, Ren Y, Xia H, Fan X and Mu Y 2010 Synthesis, structures, photoluminescent and electroluminescent properties of boron complexes with anilido-imine ligands *Inorg. Chim. Acta* **363** 1441
 - Guieu S, Cardona F, Rocha J and Silva A M S 2014 Luminescent bi-metallic fluoroborates derivatives of bulky Salen ligands *New. J. Chem.* **38** 5411
 - Sinn E and Harris C M 1969 Schiff base metal complexes as ligands *Coord. Chem. Rev.* **4** 391
 - Kubota Y, Tsuzuki T, Funabiki K, Ebihara M and Matsui M 2010 Synthesis and fluorescence properties of a pyridomethene-BF₂ Complex *Org. Lett.* **12** 18
 - Kim K B, Kim H, Song E J, Kim S, Noh I and Kim C 2013 A cap-type Schiff base acting as a fluorescence sensor for zinc(II) and a colorimetric sensor for iron(II), copper(II), and zinc(II) in aqueous media *Dalton Trans.* **42** 16569
 - Zhang X, Shi J, Song J, Wang M, Xu X, Qu L, Zhou X and Xiang H 2018 Nonconjugated fluorescent molecular cages of trinuclear fluoroborate complexes with salicylaldehyde-based Schiff Base ligands *ACS Omega* **3** 8992
 - Kilic A, Koyuncu I, Durgun M, Ozaslan I, Ibrahim H K and Ataman G 2018 Synthesis and characterization of the Hemi-Salen Ligands and their triboron complexes: spectroscopy and examination of anticancer properties *Chem. Biodiversity* **15** 1
 - Perrin D D, Armarego W L F and Perrin D R 1996 In: *Purification of Laboratory Chemicals* (New York: Pergamon) p. 48
 - Larrow J F and Jacobsen E N 1994 A practical method for the large-scale preparation of [N,N'-Bis(3,5-di-tertbutylsalicylidene)-1,2-cyclohexanediaminato(2-)]manganese(III) chloride, a highly enantioselective epoxidation catalyst *J. Org. Chem.* **59** 1939
 - Lever A B P 1984 In *Inorganic Electronic Spectroscopy* 2nd edn. (Amsterdam: Elsevier Science)
 - Fraht D, Azizi S, Ulrich G, Retaillieu P and Ziessel R 2011 Facile synthesis of highly fluorescent boranil complexes *Org. Lett.* **13** 3414
 - D'Alo A, Gachet D, Heresanu V, Giorgi M and Fages F 2012 Efficient NIR-light emission from solid-state complexes of boron difluoride with 2'-hydroxychalcone derivatives *Chem. Eur. J.* **18** 12764
 - Li H Y, Chi Z Q, Zhang X Q, Xu B Q, Liu S W and Zhang Y 2011 New thermally stable aggregation-induced emission enhancement compounds for non-doped red organic light-emitting diodes *Chem. Commun.* **47** 11273
 - Ren Y, Liu X, Gao W, Xia H, Ye L and Mu Y 2007 Boron complexes with chelating anilido-imine ligands: synthesis, structures and luminescent properties *Eur. J. Inorg. Chem.* **2007** 1808
 - Lavis L D and Raines R T 2014 Bright building blocks for chemical biology *ACS Chem. Biol.* **9** 855
 - Zhang D, Wen Y, Xiao Y, Yu G, Liu Y and Qian X 2008 Bulky 4-tritylphenylethynyl substituted boradiazaindacene: pure red emission, relatively large Stokes shift and inhibition of self-quenching *Chem. Commun.* **39** 4777
 - Sen P, Atmaca G Y, Erdogmus A, Kanmazalp S D, Dege N and Yildiz S Z 2018 Peripherally tetra-benzimidazole units-substituted zinc(II) phthalocyanines: synthesis, characterization and investigation of photophysical and photochemical properties *J. Lumin.* **194** 123
 - Lugovik K I, Eltyshv A K, Suntsova P O, Smoluk L T, Belousova A V, Ulitko M V, Minin A S, Slepukhin P A, Benassi E and Belskaya N P 2018 Fluorescent boron complexes based on new N,O-chelates as promising candidates for flow cytometry *Org. Biomol. Chem.* **16** 5150
 - Wu Y, Li Z, Liu Q, Wang X, Yan H, Gong S, Liu Z and He W 2015 High solid-state luminescence in propeller-shaped AIE-active pyridine-ketoiminate-boron complexes *Org. Biomol. Chem.* **13** 5775
 - Jenekhe S A and Osaheni J A 1994 Excimers and exciplexes of conjugated polymers *Science* **265** 765
 - Alcaide M M, Santos M F F, Pais F V, Carvalho J I, Collado D, Perez-Inestrosa E, Arteaga F J, Bosca F, Gois M P P and Pischel U 2017 Electronic and functional scope of boronic acid derived salicylidenehydrazone (BASHY) complexes as fluorescent dyes *J. Org. Chem.* **82** 7151
 - Jędrzejewska B, Grabarz A, Bartkowiak W and Ośmiałowski B 2018 Spectral and physicochemical properties of difluoroboranyls containing N,N-dimethylamino group studied by solvatochromic methods *Spectrochim. Acta Part A* **199** 86