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Synthesis and spectroscopic study of highly fluorescent β -enaminone based boron complexes



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Synthesis of novel boron complexes bearing β -enaminone ligand.
- Highly fluorescent in solvents as well as in solid state with large Stokes shift.
- These boron complexes exhibits excellent thermal and photostability.
- Electrochemical study reveals better electron transport ability compared to Alq_{3.}

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$A \hspace{0.1in} B \hspace{0.1in} S \hspace{0.1in} T \hspace{0.1in} R \hspace{0.1in} A \hspace{0.1in} C \hspace{0.1in} T$

The newly synthesized 1, 1, 2-trimethyl-1*H* benzo[e]indoline based β -enaminone boron complexes exhibited the intense fluorescence ($F_{max} = 522-547$ nm) in solution as well as in solid state ($F_{max} = 570-586$ nm). These complexes exhibited large stoke shift, excellent thermal and photo stability when compared to the boron dipyrromethene (BODIPY) colorants. Optimized geometry and orbital distribution in ground states were computed by employing density functional theory (DFT). The cyclic voltammetry study revealed the better electron transport ability of these molecules than current electroluminescent materials like tris(8-hydroxyquinoli-nato)-aluminium (Alq₃) and BODIPY, which can find application in electroluminescent devices.

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Introduction

Organoboron complexes are one of the most important types of fluorescent dyes. Remarkably, boron dipyrromethene (BODIPY) dyes [1-4], have attracted significant attention due to their excellent optical properties with high fluorescence quantum yields, high molar extinction coefficients, sharp absorption bands, high photo and chemical stability [5]. BODIPY dyes are widely used in biolabeling [6,7], as a chemosensors [8–14], as sensitizers for

dye-sensitized solar cells [15,16], as donor materials for bulk hetero-junction solar cells [17,18], and in photodynamic therapy [19,20]. BODIPY's are rarely used as electroluminescent material due to their small Stokes shifts leading to self-quenching and measurement error due to excitation and scattering of light [21,22]. High planarity of BODIPY dyes also leads to stacking of molecules causing quite strong inter molecular interactions resulting in the concentration quenching in the solid state [23–27]. Hence, they hardly exhibit fluorescence in the solid state [28]. Poor photostability of the BODIPY is one of the major disadvantage for their practical application in electroluminescence and lasers [29–32]. Other than BODIPY NBF₂N [33,34], NBF₂O [35–38], OBF₂O [39,40], and NBF₂S [41] moieties have also asymmetrically chelated BF₂ moiety.

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The BF₂ chelation enhances the electron-withdrawing property as well as the π -electron delocalization. Hence, these compounds show long-wavelength absorptions and high electron affinity [42]. Emissive solids are highly demanded for various applications, including photoelectric conversion and OLED [43–45].

In the present work, we report the synthesis and photophysical properties of 1,1,2-trimethyl-1H-benzo[e]indole based boron complexes bearing β -enaminone ligands, which shows the intense fluorescence in solvents as well as in solid state with large Stokes shift. Two methyl groups in 1,1,2-trimethyl-1H-benzo[e]indole moiety decrease the inter molecular interaction, thereby avoiding the re-absorption and self-quenching [46–48]. This gives rise to more spaced packing in the solid state, resulting in solid state luminescence with the excellent photostability.

Experimental

Materials and methods

All reagents and other chemicals were obtained from commercial suppliers and used without further purification. Nuclear magnetic resonance spectra were recorded on Bruker 300 MHz or Varian 300M instruments with TMS as an internal standard. Fluorescence spectra were performed with a Varian Cary Eclipse fluorescence spectrofluorometer at room temperature. Thermogravimetric analysis carried out on the Thermo Q-600 instrument. Electrochemical properties investigated on the CHI instrument. ESI-MS analysis performed on Varian mass spectrometer. UV–Visible spectra were performed with a Perkin-Elmer Lamda-25 spectrophotometer at room temperature.

Synthesis of the β -enaminone ligands Compound (**3a–3e**) and their boron complexes

1,1,2-Trimethyl-1*H*-benzo[e]indole (**1**) was synthesised by previously reported method by using methyl isopropyl ketone and 2-naphthylhydrazine [49].

Synthesis of (Z)-2-(1,1-dimethyl-1H-benzo[e]indol-2(3H)-ylidene)-1-phenylethanone (**3a**)

Sodium hydride (60 wt% in oil, 1.6 g, 40 mmol) was added to a toluene (100 mL) solution of 1,1,2-trimethyl-1*H*-benzo[e]indole **1** (2.1 g, 10 mmol and ethyl benzoate **2a** (1.5 g, 10 mmol) at room temperature. The solution was refluxed for 1 day. After cooling to $0-5 \,^{\circ}$ C, aq. NH₄Cl was added to the reaction mixture and extracted with ethyl acetate. The extract was dried over MgSO₄ and concentrated in vacuo. Column chromatography of the residue on silica gel gave **1** (2.6 g, 72%) as a yellow solid. mp (110–112 °C).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 12.12(s,1H), 8.03(m, 3H), 7.88(d, *J* = 8.1 Hz, 1H), 7.8(d, *J* = 8.7 Hz, 1H), 7.5(m, 4H), 7.36(t, *J* = 8.1 Hz, 8.1, 1H), 7.30(d, *J* = 8.4 Hz, 1H), 6.22(s, 1H), 1.77(s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 189.51, 175.78, 140.09, 139.93, 131.18, 130.85, 129.92, 129.81, 129.47, 129.26, 128.41, 127.33, 126.96, 123.98, 121.84, 112.03, 87.33, 49.60, 27.20. Mass (EI): C₂₂H₁₉NO calculated 313.4(M+), found 314.7(M+1).

(Z)-1-(4-chlorophenyl)-2-(1,1-dimethyl-1H-benzo[e]indol-2(3H)ylidene)ethanone (**3b**)

3b obtained from **1** and **2b** (1:1 eq) using same procedure as for **3a**.

Yield (84%). m.p. (140–142 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 12.08(s, 1H enolic), 7.99(d, *J* = 8.7 Hz, 2H), 7.93(d, *J* = 8.4 Hz, 2H), 7.8(d, *J* = 8.4 Hz, 1H), 7.79(d, *J* = 8.7 Hz, 1H), 7.51(m, *J* = 8.4, 1.5 Hz, 2H), 7.43(d, *J* = 9 Hz, 2H), 7.36(m, *J* = 8.1, 8.1, 1.2 Hz, 1H), 7.29(d, *J* = 8.4, 1H), 6.14(s, 1H), 1.75(s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 187, 176.17, 139.71, 138.38,

137.30, 130.92, 129.91, 129.86, 129.46, 128.71, 128.61, 127.03, 123.59, 121.83, 111.99, 86.93, 49.70, 27.11. Mass (EI): $C_{22}H_{18}CINO$ calculated 347.8 (M+), found 348.6 (M+1).

(Z)-2-(1,1-dimethyl-1H-benzo[e]indol-2(3H)-ylidene)-1-

(4-methoxyphenyl) ethanone (**3c**)

3c obtained from **1** and **2c** (1:1 eq) using same procedure as for **3a**.

Yield (67%). mp (156–158 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 12.02(s, 1H), 7.99–8.01(m, 3H), 7.84(d, *J* = 7.8 Hz, 1H), 7.75(d, *J* = 8.7 Hz), 7.48(t, *J* = 8.1, 8.4 Hz, 1H), 7.32(t, *J* = 8.1, 8.1 Hz, 1H), 7.25(d, *J* = 8.7 Hz, 1H), 6.95(d, *J* = 8.7 Hz, 2H), 6.16(s.1H), 3.84(s, 3H), 1.73(s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 188.62, 175.19, 162.24, 140.09, 132.80, 130.75, 129.93, 129.786, 129.52, 129.3, 129.08, 126.96, 123.38, 121.85, 113.66, 112.00, 86.95, 55.46, 49.51, 27.33. Mass (EI): C₂₃H₂₁NO₂ calculated 343.4 (M+), found 344.7 (M+1).

(Z)-ethyl 4-(2-(1,1-dimethyl-1H-benzo[e]indol-2(3H)-ylidene)acetyl) benzoate (**3d**)

3d obtained from **1** and **2d** (1:1 eq) using same procedure as for **3a**.

Yield (61%). m.p. (178–180 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 12.12(s, 1H), 8.13(d, *J* = 8.4 Hz, 2H), 7.99–8.04(m, 3H), 7.87(d, *J* = 8.1 Hz, 1H), 7.80(d, *J* = 8.7 Hz, 1H), 7.52(t, *J* = 8.4, 8.4 Hz, 1H), 7.37(t, *J* = 8.1, 8.1 Hz, 1H), 7.3(d, *J* = 8.4 Hz, 1H), 6.25(s, 1H), 4.41(q, 2H), 1.76(s, 6H), 1.42(s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 188.29, 176.48, 166.25, 143.76, 139.66, 132.54, 131.00, 129.92, 129.68, 129.53, 127.21, 127.08, 123.69, 121.88, 112.06, 87.52, 61.24, 49.80, 27.07, 14.39. Mass (EI): C₂₅H₂₃NO₃ calculated 385.5 (M+), found 386.7 (M+1).

(Z)-2-(1,1-dimethyl-1H-benzo[e]indol-2(3H)-ylidene)-1-

(4(dimethylamino) phenyl)ethanone (**3e**)

3e obtained from **1** and **2e** (1:1 eq) using same procedure as for **3a**.

Yield (55%). m.p. (180–182 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 12.00(s, 1H), 7.97–8.02(m,3H), 7.86(d, *J* = 8.4 Hz, 1H), 7.76(d, *J* = 8.4 Hz, 1H), 7.49(t, *J* = 8.1, 7.8 Hz, 1H), 7.33(t, *J* = 7.8, 7.8 Hz, 1H), 7.26(d, *J* = 8.7 Hz, 1H), 6.73(d, *J* = 9.3 Hz, 2H), 6.20(s, 1H), 3.04(s, 6H), 1.76(s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 188.73, 174.10, 152.55, 140.37, 130.56, 129.90, 129.67, 129.59, 129.19, 128.79, 127.65, 126.83, 123.12, 121.80, 111.99, 111.08, 86.90, 49.29, 40.20, 27.50. Mass (EI): C₂₄H₂₄N₂O calculated 356.5 (M+), found 357.7 (M+1).

Synthesis of 8,8-difluoro-12,12-dimethyl-10-phenyl-

8,12dihydrobenzo[e][1,3,2]oxazaborinino [3,4-a]indol-7-ium-8-uide (**4a**)

Compound **3a** (626 mg, 2 mmol) was dissolved in dry dichloromethane (12 mL), triethylamine (0.5 mL, 4 mmol) and boron trifluoride diethyl ether complex (1.41 mL, 4 mmol) was added to the solution and stirred at room temperature for 5 h. Then water was added to the solution. The solution was extracted with CH_2Cl_2 . The organic layer was washed with water and dried over MgSO₄. The crude obtained, after evaporation of the solvent, was purified by silica gel column chromatography to afford compound **4a** (580 mg, 81%) as a yellow solid.

Yield (81%) m.p. (252–254 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.91–8.09(m, 6H), 7.47–7.62(m, 6H), 6.48(s, 1H), 1.78(s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 182.78, 172.77, 140.82, 134.48, 133.51, 132.68, 132.50, 130.36, 130.03, 128.86, 128.59, 127.66, 127.24, 125.27, 122.31, 115.79, 87.89, 51.67, 24.27. Mass (EI): C₂₂H₁₈BF₂NO calculated 361.2, found 361.4 (M+).

10-(4-Chlorophenyl)-8,8-difluoro-12,12-dimethyl-8,12-dihydrobenzo [e][1,3,2]oxazaborinino [3,4-a]indol-7-ium-8-uide (**4b**)

4b obtained from **3b** by the same procedure as for **4a**.

Yield (55%) m.p. (242–244 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.94(m, 6H), 7.44–7.62(m, 4H), 6.45(s, 1H), 1.77(s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 182.75, 171.25, 140.68, 138.93, 134.60, 132.57, 131.97, 130.43, 130.04, 129.17, 128.90, 128.54, 127.31, 125.04, 122.31, 115.75, 87.95, 51.75, 24.16. Mass (EI): C₂₂H₁₇BF₂NO calculated 395.6, found 395.4 (M+).

8,8-Difluoro-10-(4-methoxyphenyl)-12,12-dimethyl-8,12dihydrobenzo[e][1,3,2]oxazaborinino[3,4-a]indol-7-ium-8-uide (**4c**)

4c obtained from 3c by the same procedure as for 4a.

Yield (41%). m.p. (246–248 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.89–8.09(m, 6H), 7.57(t, *J* = 8.1, 8.4 Hz, 1H), 7.47(t, *J* = 8.1, 8.1 Hz, 1H), 6.97(d, *J* = 9 Hz, 2H), 6.89(s, 1H), 3.87(s, 3H), 1.76(s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 182.44, 172.60, 163.50, 140.98, 134.08, 132.31, 130.25, 129.99, 129.86, 128.64, 127.14, 125.83, 125.03, 122.24, 115.66, 114.24, 86.73, 55.61, 51.46, 24.48. Mass (EI): C₂₃H₂₀BF₂NO₂ calculated 391.2, found 392.7 (M+1).

10-(4-(Ethoxycarbonyl)phenyl)-8,8-difluoro-12,12-dimethyl-8,12dihydrobenzo[e][1,3,2]oxazaborinino[3,4-a]indol-7-ium-8-uide (**4d**) **4d** obtained from **3d** by the same procedure as for **4a**.

Yield (70%). m.p. (258–260 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.17(m, 8H), 7.61(t, *J* = 8.1, 8.4 Hz, 1H), 7.51(t, *J* = 7.8, 8.2 Hz, 1H), 6.54(s, 1H), 4.42(q, 2H), 1.80(s, 6H), 1.43(t, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 182.78, 171.10, 165.84, 140.64, 137.34, 133.77, 132.68, 130.51, 130.07, 129.94, 128.53, 127.48, 127.36, 125.52, 122.36, 115.86, 88.93, 61.54, 51.86, 24.10, 14.39. Mass (EI): C₂₅H₂₂BF₂NO₃ calculated 433.3, found 433.5 (M+).

10-(4-(Dimethylamino)phenyl)-8,8-difluoro-12,12-dimethyl-8,12 dihydrobenzo[e][1,3,2]oxazaborinino[3,4-a]indol-7-ium-8-uide (**4e**) **4e** obtained from **3e** by the same procedure as for **4a**.

Yield (41%). m.p. (288–290 °C); ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.02–7.83(m, 6H), 7.55(t, *J* = 7.5, 9 Hz, 1H), 7.44(t, *J* = 6.9, 8.1 Hz, 1H), 6.71(d, *J* = 8.7 Hz, 2H), 6.31(s, 1H), 3.09(s, 6H), 1.76(s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 181.56, 173.27, 153.38, 141.39, 132.01, 130.06, 129.89, 128.70, 126.92, 124.57, 122.14, 115.57, 111.35, 85.49, 51.07, 40.19, 24.91. Mass (EI): C₂₄H₂₃BF₂N₂O calculated 404.3, found 405.6 (M+1).

Computational methodology

Theoretical calculations were perform using the Turbomole-V6.5 program [50–52] package at B3LYP (Becke, 3-parameter, Lee–Yang–Parr) [53,54]. This is most commonly used functional for reasonably accurate and precise results [55], in combination with def2-SV(P) basis set [56]. Time dependant density functional (TD-DFT) calculations were also performed with B3LYP functional and the def2-SV(P) basis set in the gas-phase.

Results and discussion

Synthesis and characterization

The β -enaminone and their boron complexes were synthesized by 1,1,2-trimethyl-1*H*-benzo[e]indole with the ethyl benzoate derivatives **2a**-**2e** in presence of sodium hydride refluxing to give β -enaminone compound **3a**-**3e** by displacing ethoxy (-OCH₂CH₃) group of benzoate ester with 1,1,2-trimethyl-1*H*-benzo[e]indole active methylene (Scheme 1). Compounds **3a**-**3e** were further treated with BF₃-etherate in dichloromethane in presence of triethyl amine as base, to give the desired organoboron compounds **4a–4e** with good yields. These compounds were column purified and characterized by mass, ¹H NMR, and ¹³C NMR spectra.

The compounds **3a–3e** were found to be present in the β -enaminone form rather than β -iminoenol or β -ketoimine. This was confirmed by the Mass spectroscopy [ESI-MS] which showed a unique fragmentation pattern by formation of $[M-Ar]^+$ ion (see Fig. S1 and Scheme S1) rather than $[ArCO]^+$ ion, this may be due to the intramolecular hydrogen bonding in β -enaminone form [57]. Also, from ¹H NMR, a peak at 6.22 ppm for an allylic proton and another peak at 12.12 ppm for the N–H proton can be observed which further confirms 100% stability in β -enaminone form because of the intramolecular hydrogen bonding. Hence the formation of $[ArCO]^+$ from the β -enaminone is least favoured [58,59]. The disappearance of the signal at 12.12 ppm for N–H proton and shifting of signal at 6.22–6.48 ppm in ¹H NMR confirms the formation of boron complex in compound (**4c**) (Fig. 1).

Thermal stability

All organoboron compounds were subjected to the thermogravimetric analysis with a ramp of 10 °C per minute from 25 to 600 °C. Compounds **4a–4e** are thermally stable up to 350 °C as shown in Fig. 2, which attributes to their good thermal stability which is favorable for OLEDs [60,61] fabrication.

UV absorption and photoluminescence property

The absorption and fluorescence spectra of the compounds **4a**-**4e** were recorded in dichloromethane as shown in Fig. 3. Compound **4e** shows maximum absorption wavelength (λ_{max}) at 454 nm, that shows bathochromic shift than the **4a** ($\lambda_{max} = 406$). The fluorescence wavelength (F_{max}) ranges from 522 to 547 nm due to π -electron delocalization and electron withdrawing property of BF₂. Surprisingly compounds **4a**-**4e** shows large stokes shift of 116, 124, 109, 129 and 64 nm, respectively. This may be due to the flexible structure of β -enaminone boron complexes in their excited states [62].

The synthesized compounds showed solid state fluorescence ranging from 570 to 586 nm as shown in Fig. 3c. The presence of methyl groups increases the steric hindrance, prevents the molecules from packing compactly, avoiding the spectral broadening. Weak molecular interactions between molecules and their large Stokes shifts provide favorable factors that eliminate self-quenching and enhance their solid state fluorescence [63].

Relative fluorescence quantum yields of compounds **4a–4e** were determined by the comparative method using known using fluorescein as a standard [64,65]. The quantum efficiency of compounds **4e** and **4c** was found to be 0.46 and 0.08, respectively. For compounds **4a**, **4b** and **4d** the quantum efficiency was found to be 0.027, 0.025 and 0.025, respectively. From the above results it is clear that the quantum efficiency for the compounds with the electron donating substituents on phenyl ring was good. Relative fluorescence quantum yields for compounds **4a–4e** are summarized in Table 1.

Electrochemical properties

Cyclic voltammetry (CV) was performed in acetonitrile solution of 0.5 mM compounds **4a–4e** along with 0.1 M tetrabutyl ammonium hexaflourophosphate as a supporting electrolyte. Platinum disk, platinum wire and Ag/Ag+ were used as working electrode, counter electrode and reference electrode, respectively. All the measurements were recorded with 100 mV/s scan rate. The cyclic voltammograms of the compound **4a–4e** shown in Fig. 4 are



Scheme 1. Synthesis of organoboron complexes 4a-4e.



Fig. 1. ¹H NMR (in CDCl₃) chemical shifts comparison for the β -enaminone **3c** and organoboron **4c**.

obeying the quasi reversible nature. The onset of oxidation potentials are 1.11, 1.02, 1.02, 1.07 and 0.5 vs. Fc/Fc^+ for **4a** to **4e**, respectively.

The HOMO energies for all the compounds were estimated by using onset oxidation potential and Eq. (1) [66,67]. LUMO was estimated by taking the difference between band gap energy and the energy of HOMO level as shown in Eq. (3) and the obtained values are given in Table 2.

$$E_{\text{HOMO}} = -(E_{\text{onset}} \text{ vs } \text{Fc}^+/\text{Fc} + 5.1)\text{eV}$$
(1)

$$E_{\rm g \ opt} = 1240 / \lambda_{\rm edge} \tag{2}$$

$$E_{\rm LUMO} = E_{\rm HOMO} + E_{\rm g} \tag{3}$$

Where $E_{1/2}$ for the Fc/Fc⁺ 0.051 V and Optical band gap was calculated using Eq. (2) and the absorption band edge (λ_{edge}) of the compounds **4a–4e** was summarized in Table 2.

The HOMO and LUMO energy levels of compounds **4a**–**4e** were -6.21, -6.12, -6.12, -6.17, -5.6 and -3.72, -3.62, -3.64, -3.69, -3.20, respectively (Table 2). The LUMO energies of the compounds **4a**–**4e** are comparable to the existing electroluminescent material e.g. Alq₃ (-3.0 eV) [68] and 1,3,5,7-tetramethyl-8-



Fig. 2. Thermo-gravimetric analysis (TGA) of compounds 4a-4e.

phenyl-BODIPY (-3.05 eV) [22]. This proves that, the compounds **4a–4e** have a good electron accepting characteristic, with enhanced charge transporting properties which can be utilized as photoelectric functional material.



Fig. 3. (a) Absorption spectra in dichloromethane 1×10^{-5} M concentration. (b) Normalized fluorescence spectra of compounds **4a–4e**. (c) Solid state fluorescence spectra of compounds **4a–4e**. (d) Photographs of the solid state fluorescence in UV and visible organoboron complexes **4a–4e**.

Table 1	
Photophysical properties of compounds 4a - 4e .	

Compound	In dichloromet	Solid State				
	λ_{\max} (nm) (ε)	F _{max} (nm)	Stoke shift (nm)	$\varphi_{\rm f}$	$\lambda_{\rm max}$ (nm)	F _{max} (nm)
4a	406 (7500)	525	116	0.027	453	570
4b	409 (9200)	533	124	0.025	458	573
4c	412 (14,300)	518	109	0.08	458	570
4d	418 (3000)	543	129	0.025	469	587
4e	454 (21,200)	523	64	0.46	479	586

Photochemical stability

In order to determine the photostability of the organoboron compounds **4a–4e**, solutions in acetonitrile were subjected to the UV-irradiation (254 nm, 0.15 mW/cm²) for 500 min. It was observed that the optical density at excitation maxima, do not significantly change for all the compounds (**4a–4e**) Fig. 5. This indicates that these compounds have very good photostability than the BODIPY dyes, may due to the highly electron rich benzo-indoline moiety. However, the excellent photostabilities of organoboron compounds (**4a–4e**) are of great importance for practical applications in photo-electronics devices.

Computational study

The minimum energy optimized geometry at ground state for the compound **4a** is shown in Fig. 6. The general trend of calculated band gap, HOMO and LUMO energies are in well agreement with the experimental observed values summarized in Table 2. Compounds **4c** and **4e** show rise in HOMO and LUMO energy levels, because of the electron-donating effect of methoxy and N,Ndimethyl group, respectively. The variations in HOMO-LUMO energies and band gap are attributed due to the modification of substituents on basic skeleton.

TDDFT calculations were also performed with B3LYP functional and the def2-SV(P) basis set in gas phase. The calculated λ_{max} values are in well accordance with the experimental values. The calculated λ_{max} , the main orbital transition, and oscillator strength (*f*) are shown in Table S1. Percentage deviation between experimental absorption and vertical excitation computed by DFT [69] is found to be 0–14.5%. The compound **4e** shows maximum deviation which is 14.5%. In all the cases, absorptions are mostly due to the first transition from HOMO to LUMO and second transition from HOMO–1 to LUMO, respectively. HOMO orbitals delocalized over the naphthyl part and LUMO orbitals are delocalized over the phenacyl part of molecules (Fig. 7), which leads to effective charge transfer which may account for large stoke shift.

Conclusions

The β -enaminone compounds (**3a**–**3e**) synthesized were found to have a stable 100% enaminone form rather than ketoamine form which was confirmed by ESI-MS and ¹H, ¹³C NMR. These β -enaminone ligands formed boron complexes to give compounds (**4a**–**4e**) respectively. The synthesized boron complexes exhibit fluorescence in dichloromethane (F_{max}) ranging from 522 to 547 nm. The β -enaminone boron complex shows large stokes shifts than that of the BODIPY (64–129 nm). Furthermore, these complexes show solid state fluorescence (570–586 nm) and have excellent thermal and photostability which is beneficial for applications in OLED and fluorescent probe.



Fig. 4. Cyclic voltammograms of 4a-4e acetonitrile solution containing 0.1 mol/L Bu₄NPF₆ at a scan rate of 100 mV/s.

Table 2Electrochemical properties of the compounds 4a-4e.

Compound	$\lambda_{edge}^{a}(nm)$	E_{g}^{a} (eV)	E°_{onset} vs Fc/Fc ⁺ (V)	HOMO ^b	LUMO ^c	HOMO ^d	LUMO ^d	$E_{\rm g}^{\rm d}$ (eV)
4a	498	2.49	1.11	-6.21	-3.72	-5.74	-2.37	3.37
4b	496	2.5	1.02	-6.12	-3.62	-5.81	-2.50	3.31
4c	499	2.48	1.02	-6.12	-3.62	-5.58	-2.19	3.39
4d	501	2.48	1.07	-6.17	-3.69	-5.83	-2.50	3.34
4e	517	2.4	0.5	-5.6	-3.2	-5.30	-1.99	3.31

^a UV–Vis spectroscopy measurements absorption spectra λ_{edge} (nm), Optical band gap calculated from the absorption band edge of the compound, $E_{g opt} = 1240/\lambda_{edge}$. ^b HOMO energy was calculated from CV using Eq. (1).

^c LUMO was estimated from the onset potential of cyclic voltammetry and band gap obtained by UV-Vis as shown in Eq. (2).

^d Theoretically calculated using DFT.



Fig. 5. Change of optical density of 4a-4e at the absorption maximum wavelength with the irradiation time. Solutions of compounds 4a-4e in Acetonitrile were irradiated under (0.15 mW/cm²) UV light (emitting at 254 nm).



Fig. 6. (a) Front view. (b) Top view. Optimized geometry of 4a.



Fig. 7. Molecular orbital energy diagram and isodensity surface plots of the HOMO-1, HOMO, LUMO and LUMO+1 of 4a-4e, calculated at the B3LYP/def2-SV(P) level of theory.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2015.03.044.

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