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Synthesis of boron-dipyrromethene–ferrocene conjugates

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ABSTRACT

Synthesis, spectral, electrochemical and photophysical properties of four BODIPY–ferrocene conjugates in which one or two ferrocenyl groups were covalently connected either directly to boron-dipyrromethene framework or to *meso*-phenyl group of boron-dipyrromethene unit are described. The BODIPY–ferrocene conjugates were prepared by adopting different synthetic routes. The absorption studies indicated the presence of charge transfer band in BODIPY–ferrocene conjugates in which the ferrocenyl group(s) were directly connected to boron-dipyrromethene framework. The electrochemical studies on conjugates indicated that ferrocenyl group was difficult to oxidize whereas boron-dipyrromethene unit was easier to reduce. The conjugates were non-fluorescent due to electron transfer from ferrocene to boron-dipyrromethene unit. However, when ferrocene was oxidized to ferrocenium ion with an oxidizing agent, the conjugates exhibited fluorescence with decent quantum yields (0.17–0.31) and lifetimes (3.8–5.2 ns).

1. Introduction

Compounds containing both a chromophore and a redox group incorporated into a single molecule have extensively been studied with great interest for applications in molecular electronic devices [1]. Ferrocene groups have been used as redox responsive unit due to its stability, ease of functionalization and well-defined electrochemistry [2]. Boron-dipyrromethenes (BODIPYs) are currently attracting multifaceted interest in many research areas owing to their advantageous photophysical properties [3]. BODIPYs are very versatile and are used as light-stable functional dyes in a variety of fields such as laser dyes, light harvesters, fluorescent switches, biomolecular labels, cation sensors and so on. The fluorescent properties of BODIPYs can be fine tuned preparatively by using several different approaches such as introduction of functional substituents on the carbon framework, enlargement of the chromophore, substitution of the fluorine atoms for O- or C-donors or replacing the *meso*-CH position with a nitrogen bridge to name few such modifications [3]. Although there are several reports on ferrocene connected chromophores such as porphyrins [4], until recently there are no reports on boron-dipyrromethene ferrocene conjugates. Recently, while our work was in progress, two independent groups [5,6] simultaneously published BODIPY dyes possessing one and two redox-active vinyl ferrocene groups at 3- and 3-, 5-positions, respectively. They demonstrated reversible electrochromism in these conjugates. In this paper, we report the synthesis of four different types of covalently linked boron-dipyrromethene–ferrocene conjugates **1**–**4** in which one or two ferrocene units are linked to boron-dipyrromethene dye at different positions of its framework (Chart 1). In these chromophore–ferrocene conjugates, it is anticipated that an intramolecular charge transfer between ferrocene and BODIPY may occur which results in (1) the appearance of charge transfer absorption band in the visible region and (2) complete quenching of the fluorescence of the chromophore. The absorption studies clearly indicate the presence of intramolecular charge transfer band in the visible region in three BODIPY–ferrocene conjugates **1**–**3** in which the ferrocene group is attached directly to the boron-dipyrromethene framework whereas the charge transfer band was not observed for BODIPY–ferrocene conjugate **4** in which the ferrocene group is attached to *meso*-phenyl group of boron-dipyrromethene unit. Interestingly, the charge transfer band in **1**–**3** disappears on oxidation of ferrocene to ferrocenium ion by oxidizing agent and at the same time, the fluorescence of BODIPY unit is restored as shown in this paper.

2. Results and discussion

The BODIPY–ferrocene conjugates **1**–**4** were synthesized by following different routes as outlined in Scheme 1. To synthesize 3-ferrocenyl boron-dipyrromethene **1**, we need an access to 3-bromo-8-(*p*-tolyl) boron-dipyrromethene **5** which was prepared in sequence of steps in one pot reaction (Scheme 2). The 3-bromo-8-(*p*-tolyl)dipyrromethane, an intermediate precursor, was prepared by treating one equivalent of *meso*-(*p*-tolyl)dipyrromethane [7] **10** with one equivalent of *N*-bromosuccinimide in THF at −78 °C in inert atmosphere under stirring for 1 h. The reaction mixture was brought to room temperature and treated with one equivalent of DDQ in open air for 10 min. The crude compound was subjected

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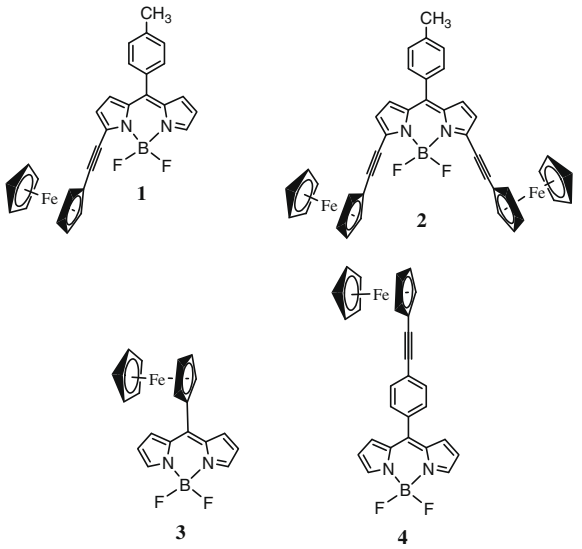
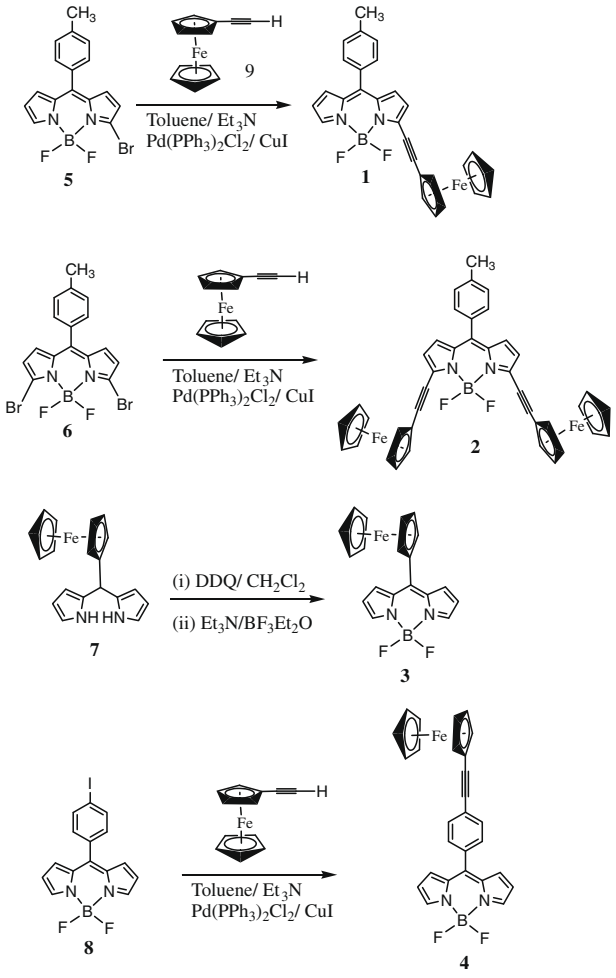


Chart 1.

to flash silica column chromatography using CH_2Cl_2 and the resulted bromo compound in CH_2Cl_2 was first treated with triethylamine followed by $BF_3{\cdot}OEt_2$ at room temperature for 1 h. Column chromatographic purification on silica afforded **5** as purple powder in 60% yield. In the last step, the compound **5** was coupled with ethynylferrocene **9** in toluene/triethylamine in the presence of catalytic amounts of CuI/$Pd(PPh_3)_2Cl_2$ at 50 °C for 4 h. Column chromatographic purification on silica afforded compound **1** as blue solid in 70% yield.



Scheme 1. Synthesis of BODIPY–ferrocene conjugates **1**–**4**.

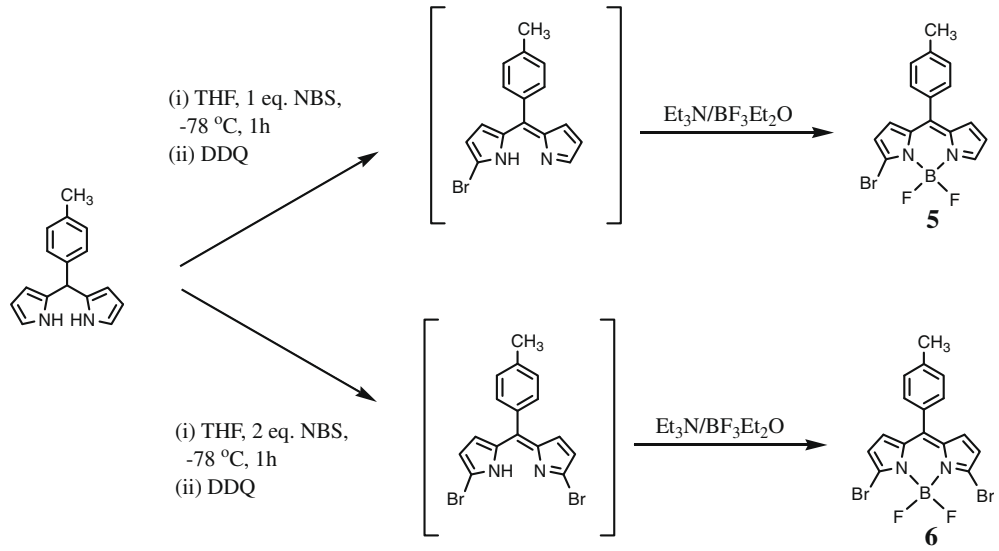
The 3,5-diferrocenyl boron-dipyrromethene **2** was prepared similarly using 3,5-dibromo *meso*-(*p*-tolyl) boron-dipyrromethene **6** as a precursor. The precursor **6** was prepared by treating *meso*-tolyldipyrromethane [7] **9** with two equivalents of *N*-bromosuccinimide to afford 3,5-dibromo-8-(*p*-tolyl)dipyrromethane, an intermediate precursor which was first oxidized with DDQ and then reacted with $BF_3{\cdot}OEt_2$. Column chromatographic purification on silica afforded pure **6** as purple powder in 64% yield. Coupling of **6** with ethynylferrocene in 1:2 ratio in toluene/triethylamine in the presence of CuI/$Pd(PPh_3)_2Cl_2$ at 60 °C for 6 h followed by silica gel column chromatographic purification afforded pure **2** as violet solid in 65% yield.

The *meso*-ferrocenyl boron-dipyrromethene **3** was prepared from *meso*-ferrocenyl dipyrromethane **7** which was prepared by following the literature procedure [8]. The compound **7** was first oxidized with DDQ in CH_2Cl_2 for 1 h, neutralized with triethylamine and reacted with $BF_3{\cdot}OEt_2$ for additional 1 h at room temperature. Column chromatographic purification on silica afforded compound **3** as green powder in 30% yield. The *meso*-[(*p*-ferrocenylethynyl)phenyl]boron-dipyrromethene **4** was prepared by coupling of *meso*-(*p*-iodophenyl)boron-dipyrromethene [9] with ethynylferrocene under same palladium coupling conditions used for the synthesis of compounds **1** and **2**. The crude compound was purified by silica gel column chromatographic purification and afforded compound **4** as orange solid in 65% yield.

The boron dipyrromethene–ferrocene conjugates **1–4** are stable and have good solubility in common organic solvents. The compounds **1–4** showed different colours in toluene as shown in Fig. 1. The compounds **1**–**4** were characterized by various spectroscopic techniques. The molecular ion peak in mass spectra and matching elemental analysis with the expected composition of compounds confirmed the identity of the compounds **1**–**4**.

In ^{1}H NMR, the signals corresponding to both BODIPY and ferrocenyl moieties are present (Fig. 2a). For e.g., the compound **3** having ferrocenyl group at *meso*-position of boron-dipyrromethene unit showed three signals at 6.54, 7.66 and 7.85 ppm corresponding three sets of pyrrole protons and the nine ferrocenyl protons were appeared as three singlets at 4.22, 4.75 and 4.97 ppm. The boron dipyrromethene–ferrocene conjugates **1**, **2** and **4** also showed similar ^{1}H NMR spectral features. All compounds showed characteristic ^{19}F NMR spectra with a quartet signal at ~ −146 ppm (Fig. 2b).

The *meso*-ferrocenyl boron-dipyrromethene **3** was also characterized by X-ray diffraction analysis (CCDC-753517). The single crystals of **3** were obtained on slow evaporation of compound **3** in CH_2Cl_2/*n*-hexane mixture over a period of one week. The compound **3** crystallizes in monoclinic with a p21/*n* space group. Fig. 3 shows the X-ray structure of **3** in two different views and the selected bond lengths and bond angles are summarized in Table 1. The structure of compound **3** shows that the boron-dipyrromethene framework, which encompasses the two pyrrole rings and the central six-membered ring containing the boron atom, is essentially planar like any other BODIPY dyes [10]. The two fluoride atoms from boron are equidistant and present above and the below the plane of the pyrrole moieties. The dihedral angle between the *meso*-ferrocenyl ring and boron-dipyrromethene ring is ~42° which is much shorter than the sterically restricted boron-dipyrromethene dyes such as *meso*-(*o*-tolyl) boron-dipyrromethene [10] in which the dihedral angle is ~ 85° indicating the presence of free rotation of *meso*-ferrocenyl group in compound **3**. This is also evident in shorter C5–C10 bond distance (1.459 Å)



Scheme 2. Synthesis of 3-bromo- and 3,5-dibromo BODIPYs **5** and **6**.

Fig. 1. Photograph of compounds **1**–**4** in toluene.

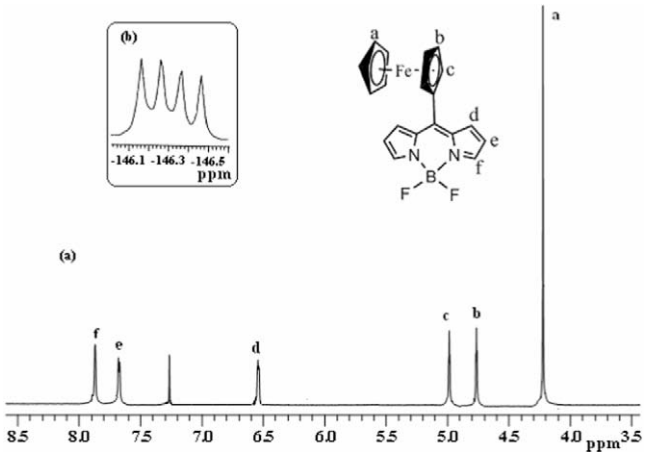


Fig. 2. (a) ^{1}H and (b) ^{19}F NMR (inset) spectra of compound **3** in selected region recorded in $CDCl_3$.

between the dipyrromethene and the ferrocenyl group compared to the sterically hindered *meso*-(*o*-tolyl) boron- dipyrromethene (1.494 Å). All other bond lengths and angles are in line with the other reported BODIPYs [10].

3. Absorption, electrochemical and fluorescence studies

The absorption spectra of compounds **1**–**4** recorded in toluene are presented in Fig. 4 and the important data is tabulated in Table 2. The compounds **1–4** showed a characteristic strong band corresponding to $S_0 \rightarrow S_1$ transition in 520–560 nm regions and one vibronic component in higher energy side. In addition, an ill-defined band at ~400 nm corresponding to $S_0 \rightarrow S_2$ transition is also present. These absorption features are in line with the other BODIPY dyes [10]. However, the most remarkable feature of the absorption spectra of BODIPY–ferrocene conjugates **1–4** with an exception of compound **4** is the presence of an additional very broad band in 600–680 nm region. This low energy band observed in compounds **1**–**3** was assigned to the intramolecular charge transfer band [5,6] which is very intense for compound **2** in which two ferrocenyl moieties are present as compared to **1** and **3** which contain one ferrocenyl moiety. This is also reflected in the intense blue colour solution of compound **2** compared to violet and brown colour solutions of compounds **1** and **3**, respectively (Fig. 1). The charge transfer band in compound **2** is observed at further red region compared to compounds **1** and **3** indicating that the charge transition is facile in compound **2**. The charge transfer transition was not observed for compound **4** in which the conjugation between the BODIPY unit and ferrocene moiety is relatively less effective unlike compounds **1**–**3** in which the charge transfer band is present because of effective conjugation between the ferrocenyl moiety and BODIPY unit. All compounds showed negligible fluorescence supporting rapid photo-induced electron transfer from donor ferrocenyl group(s) to the acceptor boron-dipyrromethene unit.

The electrochemical properties of BODIPY–ferrocene conjugates **1**–**4** were followed by cyclic voltammetry in CH_2Cl_2 using tetrabutylammonium perchlorate as supporting electrolyte. A representative cyclic voltamogram for compound **3** is shown in Fig. 5 and the data is presented in Table 2. In general, the BODIPYs show one oxidation and one reduction corresponding to the formation of monocation and mono-anion, respectively [11] In BODIPY–ferrocene conjugates **1–4**, the BODIPY unit showed one irreversible oxidation in 1.30–1.50 V region and one reversible reduction in −0.70 to −0.80 V region except for compound **4** which showed only one reduction. The reduction potential is shifted to less negative in **1**–**4** compared to free BODIPY indicating that boron-dipyrrometh-

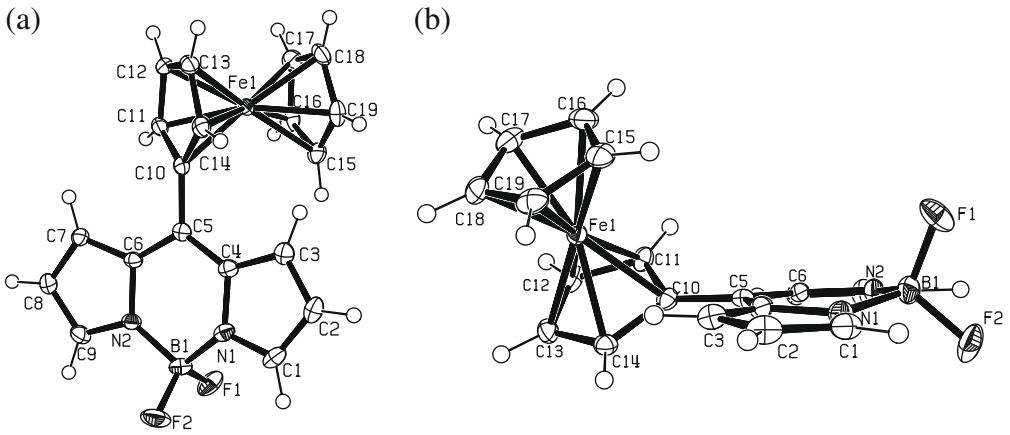


Fig. 3. X-ray crystal structure of compound **3**: (a) top view; (b) side view.

ene unit in **1**–**4** is easier to reduce. Furthermore, the conjugates **1**–**4** also exhibited a reversible oxidation corresponding to ferrocene to ferrocenium ion in 0.64–0.74 V region. The free ferrocene shows a reversible oxidation couple at 0.38 V against saturated calomel electrode which is shifted anodically by 230–360 mV in BODIPY–ferrocene conjugates **1**–**4** indicating that the ferrocenyl moiety becomes more difficult to oxidize due to distribution of electron density of ferrocene onto boron-dipyrromethene moiety in conjugates **1–4**.

Table 1
Selected bond lengths [Å] and bond angles [°] for compound **3**.

B–F1	1.388(2)
B–F2	1.386(2)
B–N1	1.540(2)
B–N2	1.543(2)
N1–C1	1.345(2)
N1–C4	1.393(2)
C4–C5	1.418(2)
C5–C6	1.412(2)
C5–C10	1.459(2)
C6–N2	1.397(2)
N2–C9	1.342(2)
N1–B–N2	105.91(13)
N1–B–F1	110.08(14)
N1–B–F2	111.28(14)
N2–B–F1	110.16(14)
N2–B–F2	110.18(15)
F1–B–F2	109.21(14)

Table 2
Photophysical and electrochemical data of compounds **1**–**4**.

Photophysical data			Electrochemical data		
Compound	$S_1 \leftarrow S_2$ λ (nm) (log ε)	C. T. band (nm) (log ε)	I E_{red} (V)	II E_{red} (V)	I E_{red} (V)
1	531 (4.67)	613_{br} (4.19)	0.641	1.57	−0.741
2	558 (4.42)	680_{br} (4.31)	0.640	1.36	−0.700
3	509 (4.88)	656_{br} (3.72)	0.743	1.56	−0.803
4	505 (4.65)	–	0.617	–	−0.709

The BODIPY dyes generally exhibit a sharp and strongly fluorescent band at ~520 nm with high quantum yields [10]. Interestingly the fluorescence of BODIPY in compounds **1**–**4** is completely quenched due to electron transfer from ferrocene moiety to BODIPY unit. However, the fluorescence of BODIPY in conjugates **1**–**4** can be restored if electron transfer from ferrocene to BODIPY is eliminated. This is possible only if ferrocene unit (Fe is in +2) is oxidized to ferrocenium ion (Fe is in +3) in conjugates **1–4**. The oxidation of Fe^{II} to Fe^{III} ion can be achieved by electrochemically as well as chemically. Yin et al. [5] and Ziessel et al. [6] in their independent work on vinylferrocene–BODIPY conjugates showed on/off optical switching of BODIPY unit by modulating the oxidation state of ferrocene electrochemically. Our lab is not equipped to perform

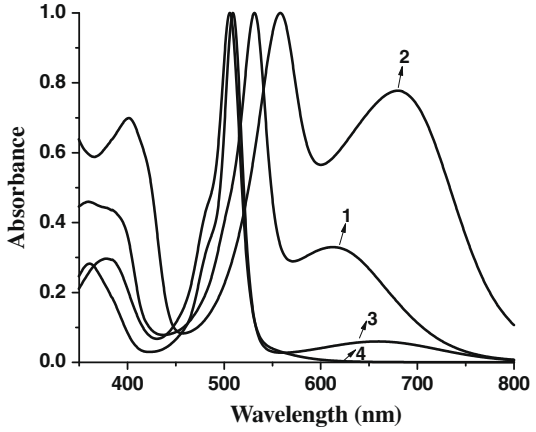


Fig. 4. Absorption spectra of BODIPY–ferrocene conjugates **1**–**4** recorded in toluene. The concentration used was 5×10^{-5} M.

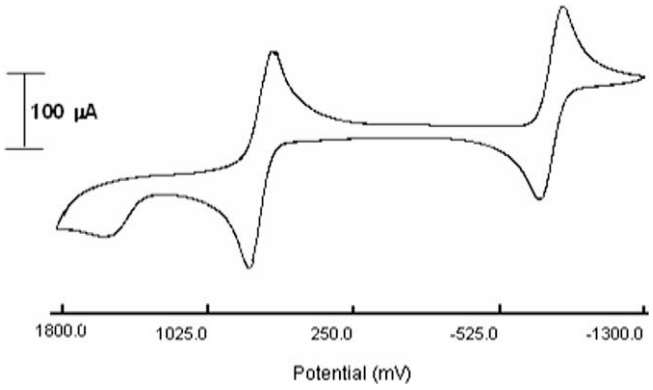


Fig. 5. Cyclic voltammogram of compound **3** in dichloromethane containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV s^{-1} scan speed.

spectroelectrochemical studies on these BODIPY–ferrocene conjugates hence we followed the changes occured in absorption and fluorescence spectra of BODIPY unit in conjugates **1** and **2** by oxidizing ferrocene to ferrocenium ion using oxidizing agent. The absorption spectral changes of compound **2** on titration with increasing concentration of $Fe(ClO_4)_3$ is shown in Fig. 6a. On addition of $Fe(ClO_4)_3$ to compound **2** which oxidizes ferrocene to ferrocenium ion, the charge transfer band present at 682 nm decreases in intensity and slowly disappears completely whereas the S0→S1 band increases in intensity, broadens and shifts to higher wavelength with a isosbestic point at 640 nm. Similar observations were made when we titrated compound **1** with $Fe(ClO_4)_3$.

These observations were further supported by steady state fluorescence studies of compounds **1** and **2** on titration with $Fe(ClO_4)_3$. The fluorescence spectra of compound **2** in toluene on titration with increasing amounts of $Fe(ClO_4)_3$ is shown in Fig. 6b. As clear from Fig. 6b that on addition of $Fe(ClO_4)_3$, the fluorescence of BODIPY unit which was quenched by ferrocene due to electron transfer is restored and shows strong fluorescence band at 612 nm and a shoulder at lower wavelength region. The calculated quantum yield and the singlet state lifetime are 0.31 and 5.2 ns, respectively for the completely oxidized compound **2** in toluene. Thus, by oxidizing the ferrocene to ferrocenium ion in **2** eliminates the possibility of electron transfer quenching of the fluorescence of BODIPY by ferrocene hence the BODIPY unit exhibits fluorescence. These observations were also clearly reflected in the colour of the solution of compound **2** in toluene which changes from intense blue to the fluorescent red. Similar observations were made with compound **1**. Thus, the preliminary titration studies of BODIPY–ferrocene conjugates with $Fe(ClO_4)_3$ clearly indicate that these compounds can be used as chemically induced switches by using appropriate oxidizing and reducing agents.

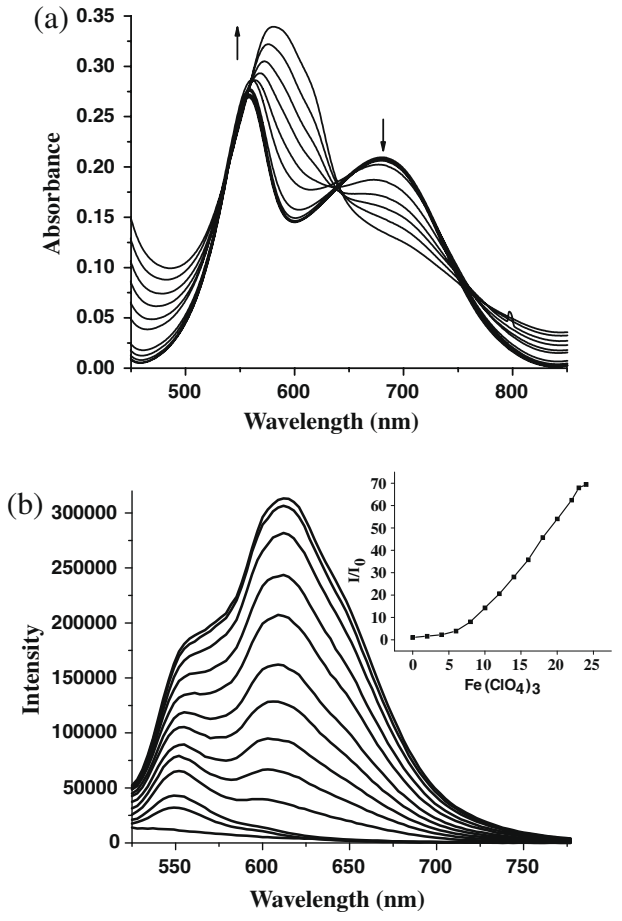


Fig. 6. (a) The absorption spectral changes of **2** (10 μM) on addition of $Fe(ClO_4)_3$ in toluene. The $Fe(ClO_4)_3$ concentration was varied from 0 to 120 μM. (b) Fluorescence spectral changes (λ_{ex} = 505 nm) of **2** (10 μM) on the addition of $Fe(ClO_4)_3$ in toluene. The concentration of $Fe(ClO_4)_3$ was varied from 0 to 240 μM. The inset show the plot of I/I_o as a function of concentration of $Fe(ClO_4)_3$.

4. Conclusions

In summary, we synthesized three monoferrocenyl–BODIPY conjugates in which the ferrocenyl group was connected to BODIPY at 3-position, 8-position and at *para* position of *meso*-phenyl group and one diferrocenyl–BODIPY conjugate in which the two ferrocenyl groups were linked at 3 and 5 positions by using appropriate synthetic routes. The NMR study indicates that the ferrocene and BODIPY units interact weakly. The absorption studies of ferrocene–BODIPY conjugates showed typical absorption features like any unsubstituted BODIPY compounds. An additional charge transfer band is also present in visible region in three out of four ferrocene–BODIPY conjugates reported here. The intensity of charge transfer band directly gave the measure of electron transfer from ferrocene to BODIPY unit in these conjugates. The electrochemical studies indicate that the ferrocene unit is difficult to oxidize and the BODIPY unit is easier to reduce in BODIPY–ferrocene conjugates. These compounds did not show any fluorescence due to electron transfer from ferrocene to BODIPY unit. However, upon oxidation of ferrocene to ferrocenium ion by using oxidizing agent, these compounds exhibit decent fluorescence due to elimination of the possibility of electron transfer in ferrocene–BODIPY conjugates.

5. Experimental

5.1. General experimental section

The ^1H spectra were recorded using Varian VXR 300 spectrometer operating at the appropriate frequencies using TMS as internal reference. referred to ^1H (of residual proton; δ 7.26) signal of $CDCl_3$. Absorption and steady state fluorescence spectra were obtained with Perkin–Elmer Lambda-35 and PC1 photon counting spectrofluorometer manufactured by ISS, USA instruments, respectively. The time resolved fluorescence decay measurements were carried out at magic angle using a picosecond diode laser based time correlated single photon counting (TCSPC) fluorescence spectrometer from IBH, UK. All the decays were fitted to single exponential. The good fit criteria were low chi-square (1.0) and random distributions of residuals. Cyclic voltammetric (CV) studies were carried out with BAS electrochemical system utilizing the three electrode configuration consisting of a Glassy carbon (working electrode), platinum wire (auxillary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Half wave potentials were measured using DPV and also calculated manually by taking the average of the cathodic and anodic peak potentials. The ES-MS spectra were recorded with a Q-Tof micro mass spectrometer. MALDI-TOF spectra were obtained from Axima-CFR manufactured by Kratos analyticals. $BF_3{\cdot}Et_2O$, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were used as obtained. All other chemicals used for the synthesis were reagent grade unless otherwise specified. Column chromatography was performed on silica (60–120 mesh).

The single crystals of compound **3** (CCDC-753517) were obtained from slow evaporation of *n*-hexane/CH_2Cl_2 solution. The intensity data collection for compound **3** have been carried out on a Nonius MACH3 four circle diffractometer at 293 K. Structure solution for the compound **3** was obtained using direct methods

(SHELXS-97) [12] and refined using full-matrix least-squares methods on F^2 using SHELXL-97 [13].

5.1.1. 3-Bromo-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (**5**)

This compound was prepared in sequence of steps in one pot reaction. *Meso*-(*p*-tolyl)-dipyrromethane **10** (500 mg, 2.12 mmol) was treated with one equivalent of *N*-bromosuccinimide (377 mg, 2.12 mmol) in dry THF (50 mL) at −78 °C under nitrogen for 1 h. The reaction mixture was warmed to room temperature and DDQ (483 mg, 2.12 mmol) in THF was added dropwise over 10 min. The solvent was removed on rotary evaporator under vacuum. The crude compound was subjected to flash column chromatography using CH_2Cl_2, concentrated on rotary evaporator, dissolved in CH_2Cl_2, neutralized with triethylamine (10.49 mL, 75.4 mmol) and treated with $BF_3{\cdot}Et_2O$ (13.44 mL, 107.0 mmol) at room temperature for additional 1 h. The reaction mixture was washed successively with 0.1 M NaOH solution and water. The organic layers were combined, dried over Na_2SO_4, filtered, and evaporated. The TLC analysis of crude compound showed three spots; the first minor spot corresponding to unsubstituted boron-dipyrromethene, the second major spot corresponding to the required 3-bromo derivative of BODIPY **5** and the last minor spot corresponding to 3,5-dibromo substituted boron-dipyrromethenes. The crude compound was subjected to silica gel column chromatography and the required 3-bromo derivative of BODIPY **5** was collected as second band using of petroleum ether/dichloromethane (90:10). The solvent was removed on rotary evaporator under vacuo and afforded pure **5** as purple powder (457 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.47 (s, 3H; CH_3), 6.53 (m, 2H; Py), 6.57 (m, 2H; Py), 6.84 (d, ^3J(H, H) = 4.28 Hz, 2H; py), 6.93 (d, ^3J(H, H) = 3.70 Hz, 2H; py), 7.38 (d, ^3J(H, H) = 7.95 Hz, 2H; Ar), 7.44 (d, ^3J(H, H) = 7.95 Hz, 2H; Ar); ES-MS: ($C_{16}H_{13}BBrF_2N_2$) 341.09 [M^+−F]; CHN calc.: C-53.23, H-3.35, N-7.76, Obsd. C-53.58, H-3.99, N-7.70.

5.1.2. 3,5-Dibromo-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (**6**)

This compound **6** was prepared by following the same procedure mentioned for **5** using two equivalents of *N*-bromosuccinimide instead of one equivalent used for the preparation of **5**. The TLC analysis showed two spots corresponding to 3-bromo derivative of boron-dipyrromethene **5** as minor spot and the desired 3,5-dibromo derivative of BODIPY **6** as major spot. The crude compound was subjected to silica gel column chromatography and the pure compound **6** was collected as second band using of petroleum ether/dichloromethane (85:15). The solvent was removed on rotary evaporator under vacuo and afforded **6** as purple powder (600 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.46 (s, 3H; CH_3), 6.53 (d, ^3J(H, H) = 4.28 Hz, 2H; Py), 6.82 (d, ^3J(H, H) = 4.28 Hz, 2H; Py), 7.32 (d, ^3J(H, H) = 7.9 Hz, 2H; Ar), 7.38 (d, ^3J(H, H) = 7.9 Hz, 2H; Ar); ES-MS: ($C_{16}H_{11}BBr_2F_2N_2$) 421.06 [M^+−F]; CHN clcd: C-43.69, H-2.52, N-6.37, Obsd. C-43.60, H-3.99, N-7.41.

5.1.3. 3-Ferrocenylethynyl-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (**1**)

Samples of **5** (50 mg, 138 μmol) and ethynylferrocene (29 mg, 138 μmol) was dissolved in toluene/triethylamine (20 mL, 5:1) and nitrogen was purged for 10 min. The coupling reaction was initiated by addition of catalytic amounts of CuI (2.6 mg, 13.8 μmol) and $Pd(PPh_3)_2Cl_2$ (5.9 mg, 8.28 μmol) and the reaction mixture was stirred at 50 °C for 4 h. The reaction progress was followed by TLC analysis at frequent intervals. The TLC analysis showed the disappearance of starting materials and appearance of new spot corresponding to the desired compound **1**. The crude compound was subjected to silica gel column chromatography using of petroleum ether/dichloromethane (80:20) and afforded **1** as blue solid in 70% yield (46 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.47 (s, 3H; CH_3), 4.34–4.37 (m, 7H; Fc), 4.67 (s, 2H; Fc), 6.53 (m, 1H; Py), 6.63 (d, ^3J(H, H) = 3.98 Hz, 1H; Py), 6.90 (m, 2H; Py), 7.32 (d, ^3J(H, H) = 7.6 Hz, 2H; Ar), 7.44 (d, ^3J(H, H) = 7.94 Hz, 2H; Ar); 7.94 (s, 1H; Py), ^{19}F NMR ($CDCl_3$): −146.3 [q, J(B, F)]; MALDI-TOF: ($C_{28}H_{27}BF_2N_2Fe$) 474.1[M^+−F], UV–vis (in toluene, λ_{max}/nm, log ε/mol^{-1} dm^3 cm^{-1}): 531 (4.67), 613$_{br}$ (4.19); CHN calc.: C-68.61, H-4.32, N-5.72, Obsd. C-53.58, H-3.77, N-7.72.

5.1.4. 3,5-bis(ferrocenylethynyl)-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (**2**)

Samples of compound **6** (50 mg, 113 μmol) and ethynylferrocene (24 mg, 113 μmol), were coupled in the presence of CuI (2.1 mg, 11.3 μmol), and $Pd(PPh_3)_2Cl_2$ (4.8 mg, 6.78 μmol) in toluene/triethylamine at 60 °C for 6 h under inert atmosphere. Column chromatographic purification on silica gel using petroleum ether/dichloromethane (70:30) afforded **2** as violet solid (51 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.46 (s, 3H; CH_3), 4.35–4.38 (m, 7H; Fc), 4.69 (s, 2H; Fc), 6.63 (d, ^3J(H, H) = 4.28 Hz, 1H; Py), 6.84 (d, ^3J(H, H) = 4.28 Hz, 1H; Py), 7.32 (d, ^3J(H, H) = 7.94 Hz, 2H; Ar), 7.42 (d, ^3J(H, H) = 7.94 Hz, 2H; Ar); ^{19}F NMR ($CDCl_3$): −146.5 [q, J(B, F)]; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): 21.6, 70.1, 70.7, 72.4, 80.4, 103.6, 123.5, 127.8, 129.2, 129.8, 130.4, 130.7, 131.6, 135.3, 136.6, 140.7; MALDI-TOF: ($C_{40}H_{29}BF_2N_2Fe_2$) 698.1 [M+1]$^+$; UV–vis (in toluene, λ_{max}/nm, log ε/mol^{-1} dm^3 cm^{-1}): 558 (4.42), 680$_{br}$ (4.31); CHN calc.: C-68.95, H-4.66, N-3.92, Obsd. C-68.58, H-4.01, N-3.99.

5.1.5. 4,4-Difluoro-8-(ferrocenyl)-4-bora-3a,4a-diaza-s-indacene (**3**)

Sample of *meso*-ferrocenyl dipyrromethane **7** (300 mg, 0.91 mmol) was taken in CH_2Cl_2 (30 mL) and oxidized with DDQ (207 mg, 0.91 mmol) at room temperature for 1 h. Triethylamine (4.86 mL, 36.4 mmol) followed by $BF_3{\cdot}Et_2O$ (5.67 mL, 45.5 mmol) was added, and continued stirring at room temperature for additional 1 h. The reaction mixture was diluted with CH_2Cl_2 and washed thoroughly with 0.1 M NaOH solution and water. The organic layers were combined, dried over Na_2SO_4, filtered, and solvent was removed on rotary evaporator under vacuum. The resulted crude product was purified by column chromatography on silica gel, using petroleum ether/dichloromethane (75:25) and afforded pure compound **3** as a green powder (102 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 4.22 (s, 5H; Fc), 4.75 (m, 2H; Fc), 4.97 (m, 2H; Fc), 6.54 (m, 2H; Py), 7.66 (m, 2H; Py); 7.85 (m, 2H; Py); ^{19}F NMR ($CDCl_3$): −146.2 [q, J(B, F)]; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): 72.1, 72.3, 74.2, 79.3, 117.6, 130.1, 134.9, 140.9, 151.8; MALDI-TOF: ($C_{19}H_{15}BF_2N_2$) 374.5 [M^+]; UV–vis (in toluene, λ_{max}/nm, log ε/mol^{-1} dm^3 cm^{-1}): 509 (4.88), 656$_{br}$ (3.72); CHN calc.: C-60.69, H-4.02, N-7.45, Obsd. C-60.58, H-3.99, N-7.70.

5.1.6. 4,4-Difluoro-8-[4-(ferrocenylethynyl)phenyl]-4-bora-3a,4a-diaza-s indacene (**4**)

Samples of *meso*-(4-iodophenyl) boron-dipyrromethene **8** (50 mg, 127 μmol) and ethynylferrocene (26 mg, 127 μmol) in dry toluene/triethylamine (3:1, 20 mL) were coupled in the presence of catalytic amounts of CuI (2.4 mg, 12.7 μmol) and $Pd(PPh_3)_2Cl_2$ (5.3 mg, 7.62 μmol) at 50 °C for 6 h. The formation of the desired compound was confirmed by the appearance of new spot on TLC. The crude compound was purified by silica gel column chromatography, and the pure compound **4** was collected using petroleum ether/dichloromethane (80:20) as orange solid (39 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 4.27–4.30 (m, 7H; Fc), 4.55 (m, 2H; Fc), 6.56 (m, ^3J(H, H) = 3.98 Hz, 2H; Py), 6.97 (d, ^3J(H, H) = 3.98 Hz, 2H; Py), 7.53 (d, ^3J(H, H) = 7.94 Hz, 2H; Ar), 7.62 (d, ^3J(H, H) = 8.3 Hz, 2H; Ar); ^{19}F NMR ($CDCl_3$): −146.2

[q, J(B, F)]; MALDI-TOF: ($C_{27}H_{19}BF_2N_2Fe$) 474.9 [M^+]; UV–vis (in toluene, λ_{max}/nm, log ε/mol^{-1} dm^3 cm^{-1}): 505 (4.65); CHN calc.: C-67.97, H-4.23, N-5.87, Obsd. C-67.68, H-4.09, N-5.72.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.01.009.

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